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PREDICTING ARSENIC MOBILITY
AS PART OF THE ANACONDA
SEWAGE TREATMENT
LAGOON/WATERFOWL PROJECT

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CAMP DRESSER & McKEE INC.

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SUMMARY

Installation of duck ponds on the area to the east of the Opportunity tailings ponds will provide a tractable alternative method of disposing of the town of Anaconda's primary sewage effluent. However some precautions must be taken to prevent leaching of arsenic from the soils beneath the ponds into the ground water.

The major conclusions drawn from the duck ponds evaluation are:

1. A soil arsenic concentration of 15 ug/g is likely to result in the generation of a leachate bearing 50 ug/L of arsenic at equilibrium.
2. At least the top 12 inches of soil must be removed from the area to be submerged in order to prevent significant degradation of the ground water.
3. In selected locations in the vicinity of sites 2C and 3B, soil may have to be removed to a depth of 18 inches in order to prevent ground water degradation.
4. An area to the south of transect R5 appears unsuitable for any impoundment based on elevated soil arsenic concentrations in both the 6 to 12-inch and 12 to 18-inch layers.
5. Calculations indicate that the leachate percolating through the unsaturated zone following impoundment will be diluted by a maximum of 40 percent by the upper five feet of the laterally migrating ground water aquifer. However, a zone of water will also exist above the pre-existing ground water aquifer in which no dilution will occur.



1.0 INTRODUCTION

After many years of routing raw sewage to the Anaconda Minerals Company's Opportunity Tailings Ponds, the community of Anaconda, Montana has built a primary sewage treatment facility which currently routes treated effluent onto the Opportunity tailings pond. In the original design, infiltration ponds to accept the effluent were sited near the treatment plant. However, U.S. EPA determined that material underlying the proposed location was contaminated with mineral processing wastes, and could potentially contaminate the underlying ground water. As an alternative infiltration pond site, Anaconda Minerals Company has offered the use of land northeast of the Opportunity Tailings Ponds. The Montana Department of Fish, Wildlife, and Parks and Ducks Unlimited viewed this alternative as an opportunity to create migratory waterfowl habitat in addition to providing a disposal site for effluent from the new treatment facility.

The proposed "duck ponds" would be located northeast of the Opportunity Tailings Ponds (Figure 1). Inflow to the pond would consist of primary sewage effluent from the community of Anaconda, and groundwater intercepted by the North Ditch. Outflow from the pond would be discharged via ditch and culvert to the Mill-Willow Bypass.

The proposed sewage treatment lagoon/waterfowl habitat project is located in an area which has previously been impacted by fallout from airborne emissions from the Anaconda Smelter complex, and by blowing dust and tailings. Therefore, the contact between wastewater and tailings residues should be evaluated to determine the potential for leaching of the arsenic and subsequent ground water contamination.



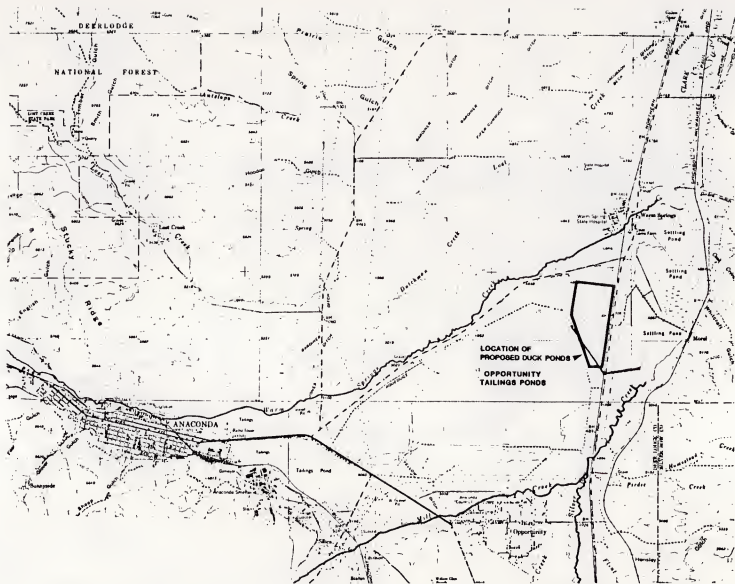


Figure 1. Map of the Anaconda Region Showing the Location of the Proposed Duck Ponds (scale: $5/8" = 1$ mile)



2.0 OBJECTIVES

The objectives of this study were:

- Phase 1a Batch shaker experiments were performed to characterize leachable arsenic concentrations from soils with a range of arsenic concentrations.
- Phase 1b A sorption experiment was conducted to define the mechanism and retentive capacity of soils for arsenic in the +5 valence state.
- Phase 1c Column tests were undertaken to determine the capability of the deeper soil horizons to alternate arsenic leached from the surficial soil layers.
- Phase II Field sampling was undertaken to define the location and extent of any pockets of high arsenic concentrations in the 6 to 12 and 12 to 18-inch soil horizons. 'High' arsenic concentrations are defined to be the soil arsenic concentration likely to leach 50 ug/L arsenic or greater into solution under field conditions of porosity and hydraulic conductivity.

Soil and wastewater samples were collected from the site for use in the Phase I laboratory experiments which were designed to determine if arsenic will be leached under anticipated field conditions. Preliminary work performed on site soils by the State of Montana (Sonderegger 1985), indicated that sufficient arsenic exists in at least the upper six inches of soil to produce leachable arsenic concentrations above the MCL of 50 ug/L. Based on this data, all parties have agreed that the top six inches of soil will have to be removed before creating the duck ponds. One objective of this study was to define the level of soil-bound arsenic in the soil below six inches that may produce leachate containing arsenic concentrations above 50 ug/L. With this information it is possible to estimate the volume of additional soil (if any) to be removed from the proposed duck ponds in order to prevent ground water degradation above the MCL. Additional soil samples were collected from the 6 to 12-inch and 12



to 18-inch horizon under Phase II to ensure that the soil remaining after removal of the top six inches will not contain leachable arsenic concentrations capable of degrading the ground water to an arsenic concentration above 50 ug/L.



3.0 LABORATORY METHODS

This section describes the methodology employed in the leach, sorption, and column tests. The data for these experiments is presented in Section 4.0.

3.1 SOIL LEACHING EXPERIMENTS

All batch shaker tests followed the procedure outlined in ASTM Method D3987-81 (Shake Extraction of Solid Waste With Water) with some modification. The ASTM Method is provided in Appendix A.

The first series of shaker tests established the length of time required for each soil horizon to reach equilibrium with the leaching fluid. This was achieved by withdrawing 4 aliquots of the leaching fluid over a 44-hour period (4, 7, 22, and 44 hr.), filtering the fluid through a 0.45 μ m filter, acidifying the filtrate with ultra-pure HCl, and analyzing the fluid for arsenic. Hydrochloric acid was used to enable speciation of arsenic into As(III)/As(V) at some future date if it is deemed necessary. Spike recoveries of arsenic in HCl acidified samples were always between 90-110 percent, indicating minimal matrix interference. Comparison with nitric acid fixed samples returned similar arsenic concentrations for any given fluid.

The first set of shaker tests showed that equilibrium was achieved quickly (Figure 2) and that anoxic conditions (under nitrogen) did not effect leaching rates or quantities. Based on these preliminary tests, the assumption was made that the sorptive capacity under oxidizing conditions was similar to that under anoxic conditions. Therefore, subsequent tests were made in an oxidizing environment.

The soils used in the second series were from the 0 to 6-inch, 6 to 12-inch, and 12 to 18-inch layers from pit 3C, from the 6 to 12-inch layer



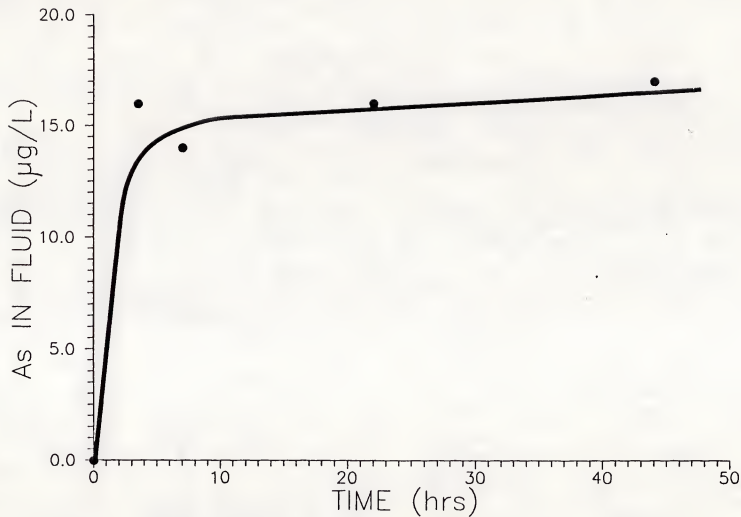


Figure 2. Arsenic concentrations in the supernatant as a function of time for the shaker experiments.



of pit 5C, from the 12 to 18-inch horizon at the 2B pit site, and from the 6-12-inch horizon of location 2B. A blank with no soil was run concurrent with the shaker experiments.

For each soil, four different ratios of soil to water were chosen, dependent upon soil porosity. These ratios were 0.25 g, 2.5 g, 12.5 g and 250 g of soil in 250 mL of the North Drain/Sewage treatment plant mixed fluid. A water mix of four parts North Drain water to one part sewage effluent was chosen based upon the predicted composition of the duck pond influent (Dick Montgomery, personal communication). The mix was used to simulate the fluid which is anticipated to interact with the soil.

After 44 hours, the experiment was terminated and the fluids and solids separated by centrifuge. The solutions were filtered through a 0.45 μ m filter and acidified with ultra-pure HCl. The data are presented in Appendix B and discussed in section 4.2.

3.2 SHAKER SORPTION EXPERIMENTS

The purpose of this experiment was to quantify the potential arsenic sink available in the calcareous soils. The soils used were the 6 to 12-inch and the 12 to 18-inch layers from pit 3C. The ratio chosen to model equilibrium interactions between soil and water was 1:100 respectively. This ratio represents the passage of approximately 300 pore volumes through the medium. The data are presented in Appendix B and discussed in Section 4.1.

An arsenic sorption isotherm was measured using arsenic spikes of 10, 25, 50, 100, 250 and 500 μ g/L. Reagent grade disodium hydrogen arsenate heptahydrate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) was used to make the spike solutions because arsenic under the redox conditions prevailing in the surface water is anticipated to be primarily in the +5 oxidation state.

The soil/water samples were was shaken and sampled after 48 hours from



initiation of the experiment. The extracted fluid was filtered and acidified with ultra-pure HCl.

3.3 COLUMN TESTS

Column tests were run following the proposed ASTM method (Draft Method for Leaching Solid Waste in a Column Apparatus, ASTM committee D34.02.02) under constant head conditions. This procedure is provided in Appendix C.

Four columns were established. As shown in Table 1, the columns consisted of assemblages representative of the horizons in pit 3. The profile in pit 3 consists of a fine grained A and B horizon underlain by a carbonate cemented gravel zone. This profile is represented by the multilayer "composite" column. Two of the columns were multilayer and two represent only one material. One of the multilayer columns (Column A) also had duck droppings added to the surface in an attempt to define the effect of an organic component.

For each column, a mix of 20 percent sewage effluent/80 percent North Drain water was passed through the column, and leachate collected. Columns were run for a maximum of 110 pore volumes. Approximately 20 percent of samples were submitted for analysis. The pore volume was measured by applying a vacuum to the top of the columns and filling the void space using the mixed fluid. As a check on this method, the columns were weighed both pre- and post-filling and the pore volume calculated assuming unit density for the mix.

Only the B and deeper soil horizons were utilized in these tests because it had already been established that at least the upper 6 inches of material in the proposed duck ponds area will be removed prior to development of the area as a wildlife refuge/sewage lagoon.



The Plexiglas columns were packed so that the soil layers were inverted. The B horizon was on the bottom, followed by gravels in the middle, and the coarser caliche layer at the top. Columns were packed to approximate field permeability determined from falling head tests in the duck pond area (Appendix D). Influent was from the base of the column and effluent was collected from the top. The rate of flow was recorded and the height of the reservoir above the effluent tube measured to allow calculation of the hydraulic conductivity (Table 1 and Appendix E). Samples were collected approximately every pore volume and analyzed for arsenic, pH, oxidation/reduction potential, temperature and specific conductivity (Appendix F). Arsenic analyses were performed using atomic absorption/graphite furnace with nickel nitrate added to suppress interferences. Selected samples were also analyzed for Ca, Fe, K, Mg, Na, alkalinity, Cl, and SO₄.

All arsenic analyses were performed by Rocky Mountain Analytical Laboratory according to CLP method 206.2 CLP-M, as specified in the work plan (EPA Document No. 228-TS1-EP-DGWC-1).



TABLE 1
SYNOPSIS OF PARAMETERS RELEVANT TO THE COLUMN EXPERIMENTS

Column I.D.	Pit	Layers (inches)	As (ug/g)	$\log K^1$ (cm/sec)	Pore Volume (mL)	No. of Pore Volumes Passed	Weight of Soils in Column (g)
A	3C	Duck Droppings	0	-3.5	650	38.5	3885
		6 - 18	16				
		18 - 24	8				
		24 - 36	5				
D	3C	12 - 18	8	-4.0	500	20	1707
X	3C	12 - 18	8	-3.6	200	88	966
		18 - 24	8				
		24 - 36	5				
Z	3C	6 - 12	30	-4.0	550	26.5	1724.1

¹ Hydraulic Conductivity



4.0 RESULTS

4.1 SORPTION EXPERIMENT

The data generated from the experiments (Appendix G) is plotted on log-log paper (Figure 3). For arsenic concentrations up to 500 ug/L, the isotherm conforms to the Freundlich (1926) equation. This is expressed as:

$$S = K_d C^b \quad \text{---(1)}$$

where:

- S = the mass of arsenic sorbed per gram of soil (at equilibrium)
- K_d = the distribution coefficient
- C_d = the equilibrium concentration of arsenic in solution (mg/L)
- b = a constant dependent on the solute species, nature of the material, etc.

Converting equation (1) to the logarithmic form gives

$$\log_{10} S = \log_{10} K_d + b \log_{10} C \quad \text{---(2)}$$

The data from Figure 3 may be expressed in the form of equation 2 as:

$$\log_{10} \text{ug/g} = 0.98 \log_{10} C + 1.29 \quad (r = 0.998 \text{ for } n = 6)$$

where:

$$\log_{10} K_d = 1.29 \text{ (19.5 mL/g)} \text{ and } b = 0.98$$

Freeze and Cherry (1979) point out that the K_d is a valid representation of partitioning of a sorbate between the solid and liquid phases only if the reactions are rapid and the isotherm is linear. The sorption experiments on the duck pond soils meet these criteria because arsenic leached from the soils during the shaker tests reached an equilibrium concentration after three hours (Figure 2) and because $b = 0.98$ for this sorption experiment.



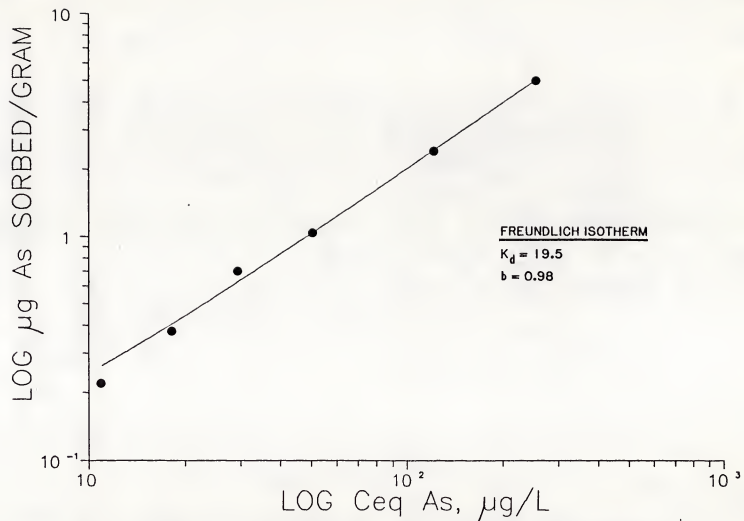


Figure 3. Log/log plot of sorption data. The line drawn through the points represents the Freundlich isotherm for the data. ($r = 0.998$)



A more generic form of the K_d is:

$$K_d = \frac{\text{ug removed from solution/gram of solid}}{\text{ug/mL at equilibrium in solution}} \quad \text{---(3)}$$

If the criteria for degradation of ground water is selected as 0.05 ug/mL, the distribution coefficient can be used to predict the mass of arsenic sorbed to the solid phase. Using equation 3, the calculated concentration is 1 ug of As sorbed per gram of solid.

Another method of interpreting the data is to calculate the percentage of As sorbed onto the solid phase as a function of the initial As concentration in solution (Figure 4). This analysis indicates that approximately 50 percent of the arsenic up to concentrations of 500 ug/L will be sorbed onto the substrate.

4.2 SHAKER TESTS

The objective of these experiments was to determine leached aqueous arsenic concentrations for a range of soil arsenic concentrations.

Batch Leaching Experiments

Figure 5 shows that a linear relationship exists between the soil arsenic concentration and arsenic leached into solution. The data are tabulated in Appendix B.

Figure 5 shows leachable arsenic concentrations in a weight (gm) to volume (mL) ratio of 1:100 soil to fluid. This ratio approximates equilibrium



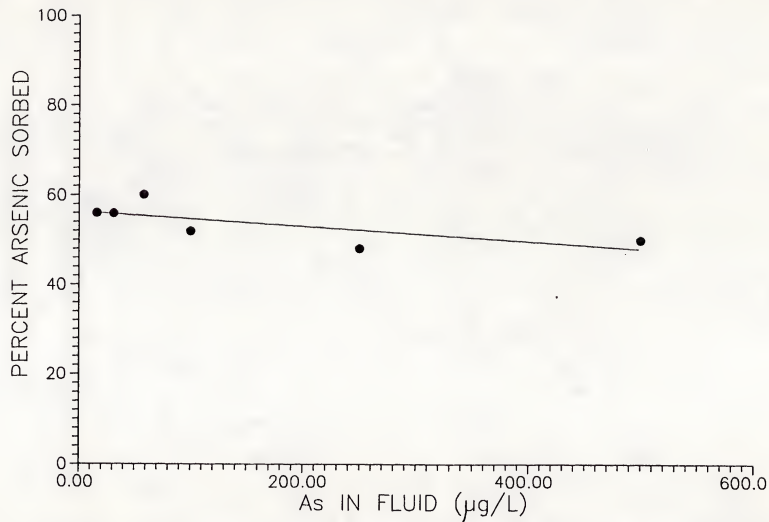


Figure 4. The percentage of arsenic sorbed as a function of the initial spike concentration.



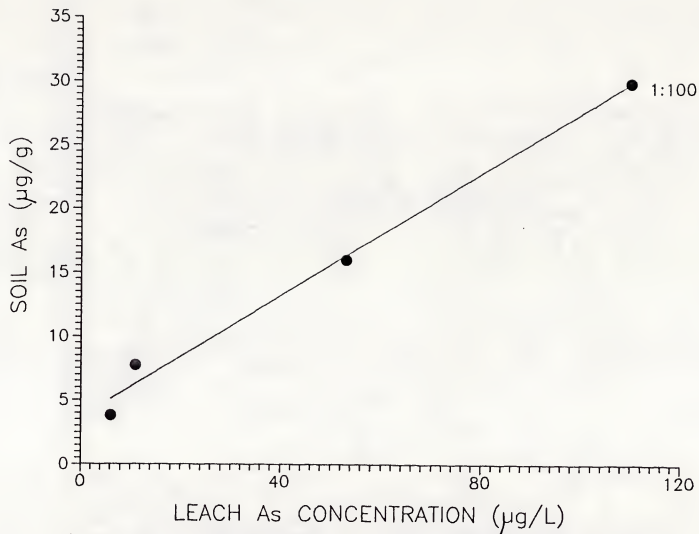


Figure 5. The relationship between soil arsenic concentration and the leachable arsenic in solution for a soil to water ratio of 1:1000.



concentrations at 300 pore volumes to simulate long term equilibrium conditions. Arsenic leaching into the interstitial water can be estimated from linear regression equation for the 1:100 curve ($r = 0.9998$):

$$\text{leachable arsenic in solution (ug/L)} = \frac{\text{soil arsenic (ug/g)} - 3.64}{0.24} \quad (4)$$

Using this equation, a soil containing an arsenic concentration of 15.6 ug/g in contact with the duck pond water will result in an equilibrium leachate concentration of approximately 50 ug/L arsenic.

4.3 COLUMN EXPERIMENTS

The objective of the column experiments was to provide a more representative test of field conditions in order to evaluate the potential of the deeper soil horizons to remove arsenic from the leachate known to release arsenic from the batch experiments.

Figure 6 shows the results of two column experiments: column X was a multiple layer column consisting of material from Pit 3C (12-36 in.) while column D was comprised exclusively of the 12 to 18-inch horizon from Pit 3C. The multiple layer column (X) contained three distinct layers of material from Pit 3C: 12-18 in., 18-24 in., and 24-36 in. packed in relative proportions as observed in the field (see Table 1). Both columns X and D contained soils from the 12 to 18-inch horizon with arsenic concentrations of 8 ug/g. The difference in the maximum concentrations of eluted arsenic from the two columns shown in Figure 6 may be attributed to the carbonate material in the 24 to 36-inch zone of column X. The caliche appears to retard arsenic in this column and to subsequently release it at lower equilibrium concentration over many pore volumes. It is noteworthy that even at the low arsenic concentration (8 ug/g) analyzed in the soils used in Column X, there is sufficient labile arsenic in the soils (Table 2) to impact the ground water.



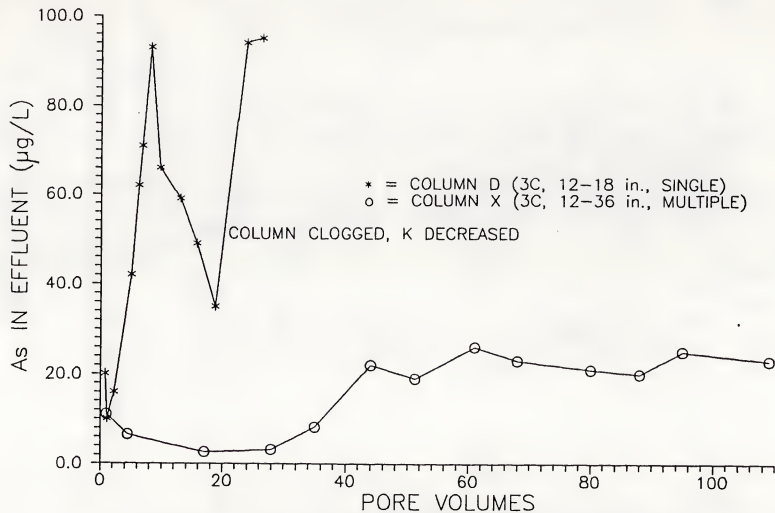


Figure 6. Arsenic concentrations in the leachates collected from Columns X and D. Note that the increase in the arsenic concentration towards the end of Column D is a result of a decrease in the hydraulic conductivity and a consequent increase in the residence time of the fluid.



ANACONDA DUCK PONDS ARSENIC DATA

BORING	X	Y	AS 6-12"	AS 12-18"	LOG 6-12	LOG 12-18
1A	1166038	805613	78	14	1.872	1.146
1B	1165547	805676	311	11	2.493	1.041
1C	1165042	805741	41	6	1.613	0.778
1D	1164579	805813	37	16	1.568	1.204
1E	1164063	805898	16	13	1.204	1.114
1F	1163565	805962	10	12	1.000	1.079
2A	1165912	804616	81	28	1.908	1.447
2B	1165419	804696	90	16	1.954	1.204
2C	1164927	804742	60	44	1.778	1.643
2D	1164425	804823	47	8	1.672	0.903
2E	1163937	804893	20	9	1.301	0.954
2F	1163405	804963	27	16	1.431	1.204
3A	1165789	803642	20	13	1.301	1.114
3B	1165288	803700	321	121	2.507	2.083
3C	1164810	803777	52	13	1.716	1.114
3D	1164289	803836	20	15	1.301	1.175
3E	1163779	803930	15	9	1.176	0.954
3F	1163221	803994	31	10	1.491	1.000
4A	1165644	802645	41	13	1.613	1.114
4B	1165191	802708	36	11	1.502	1.041
4C0	1164949	802750	26	11	1.415	1.041
4C1	1164716	803289	20	21	1.301	1.322
4C2	1164671	802994	38	14	1.530	1.146
4C3	1164656	802788	15	14	1.176	1.146
4C4	1164617	802525	25	13	1.390	1.114
4C5	1164576	802237	24	12	1.355	1.079
4C6	1164425	802834	15	6	1.176	0.778
4D	1164157	802878	24	11	1.380	1.041
4E	1163672	802950	20	17	1.301	1.230
5A	1165525	801657	90	13	1.954	1.114
5B	1165085	801707	72	16	1.867	1.204
5C	1164487	801790	4	4	0.602	0.502
5D	1163989	801863	40	7	1.602	0.843
5E	1163368	801966	16	7	1.204	0.845
6A	1165354	800663	114	34	2.057	1.531
6B	1164854	800743	109	37	2.037	1.568
6C	1164363	800810	49	20	1.690	1.301
7A	1165288	799885	29	13	1.462	1.114
7B	1164776	799970	594	61	2.774	1.785

Table 2. Arsenic concentrations in soil samples collected during the phase II portion of this study. X and Y correspond to the longitude and latitude respectively.



Figure 7 shows the results from columns A and Z which consisted of a multiple layer soil profile (6-36 in.) and material from the 6 to 12-inch profile of Pit 3C, respectively. The multiple layer column A consisted of three layers from Pit 3C: 6-18 in., 18-24 in., and 24-36 in. packed in relative proportions as observed in the field (Table 1) plus a thin layer of duck droppings to simulate the effect of organic material. Column Z contained only the 6 to 12-inch profile. The 6 to 12-inch material has a soil arsenic concentration of 30 ug/g. Effluent arsenic concentrations reached maximum of 3,200 ug/L in column Z to 490 ug/L in column A (Figure 7). The multiple layer column (A) contained the apparently sorptive 24 to 36-inch horizon in its profile which alternated arsenic resulting in lower concentrations over more pore volumes. Significant ground water degradation is possible if mix water is allowed to interact with soil arsenic concentrations at a level of 30 ug/g. The effect of organic material in column A was to produce a slightly more reducing environment based on platinum electrode measurements (Appendix F). The measured values were still sufficiently oxidizing to maintain arsenic in the +5 oxidation state (see Section 7.3).

From the results of the column experiments, it is apparent that the ground water will be impacted to some extent by the arsenic concentrations found in soils used in columns A and Z. The potential impact on the ground water by leachate emanating from the contaminated soils is examined in Section 5.2.



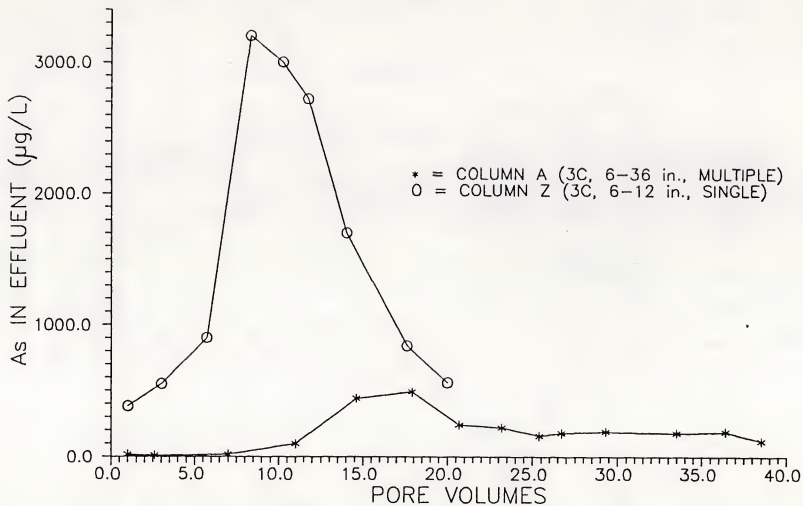


Figure 7. Arsenic concentration in the leachates collected from Columns A and Z.



5.0 DATA INTERPRETATION

5.1 RELATIONSHIP BETWEEN SHAKER, SORPTION, AND COLUMN STUDIES

The shaker tests simulate several mechanisms, including dissolution of a soluble arsenic bearing phase, desorption of surface bound arsenic and sorption of arsenic onto the substrate. The column tests combine the same phenomena but in a manner more representative of field conditions. Single horizon columns (e.g., D and Z) should be comparable to the shaker tests which used these soils.

In column D, the soil arsenic concentration was 7.8 ug/g (rounded to 8 in Table 1). Using equation 4 to predict the equivalent long term arsenic concentration results in a value of 17 ug/L. This is in good agreement with the apparent equilibrium arsenic concentration in column D effluent (23 ug/L) after 100 pore volumes (Figure 6). In column Z, the soil arsenic concentration was 30 ug/g which, using equation 4, results in a predicted equilibrium concentration of 110 ug/L. In this case, the column test has not reached equilibrium showing a leachate concentration of 180 ug/L (Figure 7). The conclusion is that the shaker test at low ratios of soil to fluid appears to model equilibrium arsenic concentrations in the single horizon column tests.

The two multiple layer column tests, A and X, can be related by the horizons absent in X but present in A. In column A, the 6 to 12-inch layer (30 ug/g) is included together with duck droppings to simulate organic material on the bottom of the ponds. These layers are absent in column X. The difference in leachable arsenic concentrations is significant due to the lack of the high As, 6 to 12-inch layer in column X. In column A, the maximum leached arsenic concentration was 490 ug/L while in column X, it was 26 ug/L (Figures 6 and 7).



5.2 PREDICTION OF SOIL ARSENIC CONCENTRATION WHICH RESULTS IN GROUND WATER DEGRADATION BELOW THE MCL

The objective of this section is to use the experimental data to define the soil arsenic concentration which will produce a leachate bearing 50 ug/L of arsenic. This section does not consider dilution of the leachate by groundwater.

5.2.1 Shaker Experiment Determination of MCL

Equation 4 can be used to estimate the soil arsenic concentration which will produce an equilibrium leachate arsenic concentration at the MCL (50 ug/L). In the long term (300 pore volumes), a sorbed soil concentration of 15.6 ug/g will produce a leachate of 50 ug/L.

5.2.2 Column Determination of MCL

As an alternative approach, the column data can be used in defining the MCL-producing soil arsenic concentration. Typically, the columns had hydraulic conductivities of 10^{-4} cm/sec, an order of magnitude lower than field conditions (10^{-3} cm/sec, Appendix D). Therefore, under actual field conditions, the amount of arsenic leached would be contained in a larger volume of water and the concentrations would decrease. The reverse of this phenomena was observed in Column D when the hydraulic conductivity decreased by a factor of three and the concentration of arsenic increased three times (see Figure 6). Therefore, the arsenic concentrations measured in effluent from the columns may be diluted by approximately ten-fold to represent the lower residence time and larger volumes of water under field conditions. The column which best simulated the field soil profile was Column A. This column produced a peak arsenic concentration of 490 ug/L and equilibrium values of 180 ug/L. Correcting these concentrations by the dilution factor would result in a field interstitial arsenic concentration of 49 ug/L (close to the MCL) and an equilibrium concentration of 18 ug/L. The soil arsenic concentrations in column A which are anticipated to yield



these arsenic concentrations in the duck pond leachate is approximately 16 ug/g. This value was determined as follows. The horizons in the column comprised duck droppings (<1 ug/g As), the 6 to 18-inch horizon (16 ug/g), the 18 to 24-inch horizon (7 ug/g) and the 24 to 36-inch horizon (5 ug/g). The contribution of the latter two horizons to leachable arsenic concentrations appears to be negligible based on the arsenic concentrations found in leachate from column X. Therefore, 16 ug/g soil arsenic is that concentration which would be predicted to impact the ground water at an arsenic concentration close to the MCL.

5.2.3 Recommended Soil Arsenic Concentration

Based on an evaluation of the shaker and column experimental data, a value of 15 ug/g is selected as a threshold soil arsenic concentration which will produce a leachate arsenic concentration of 50 ug/L.

5.3 MITIGATION OF LEACHATE ARSENIC CONCENTRATION BY GROUND WATER DILUTION

As the water from the pond infiltrates, a ground water mound will be created below the duck pond. Ultimately some of this pond water will mix with water in the ground water aquifer resulting in a dilution of the arsenic up to 40 percent. A zone of pond water above the original ground water aquifer will also exist and migrate laterally. This zone of water will remain undiluted and therefore contain arsenic concentrations equal to the leachate concentrations. The results of the hydrologic modeling are provided in more detail in Section 8.0.

5.4 ESTIMATION OF TIME OF IMPACT UPON GROUND WATER

The velocity of arsenic moving in the ground water regime can be estimated through use of the following equation.

$$\frac{V_w}{V_{As}} = R = 1 + \frac{p K_d}{n} = 161 \quad \text{---(5)}$$



where

V_v = velocity of a water molecule
 V_{As} = velocity of an arsenic molecule
 R = retardation Factor
 p = bulk density of aquifer material (estimated to be 1.6 gm/cm³)
 n = effective porosity (estimated to be 0.20)
 K_d = distribution coefficient (20 mL/g from Figure 3)

The velocity of the ground water can be estimated as the sum of the regional ground water velocity and the velocity due to the ground water mound. The regional ground water velocity is equal to:

$$V_{reg} = \frac{K \frac{dh}{dL}}{n} = 2.50 \text{ ft/day}$$

where

K = hydraulic conductivity (50 ft/day)
 $\frac{dh}{dL}$ = gradient (0.01)
 n = effective porosity (0.20)

The velocity due to the mound is equal to

$$V_m = \frac{K \frac{dh}{dL}}{n} = \frac{(50)(0.0008)}{0.20} = 0.2 \text{ ft/day}$$

Therefore the overall total velocity is approximately 2.7 feet/day. This volume can be checked by dividing the recharge (Q) due to infiltration by the affected area (A) and effective porosity (n).

$$V = \frac{Q}{A n} = \frac{24,000}{2 \times 7000 \times 5.5 \times 0.2} = 3.1 \text{ ft/day}$$

where 24,000 cubic ft/day is the calculated recharge, 7000 ft is the diameter of the mound and 5.5 is the height of the mound. The calculated



velocity agrees closely with the 2.7 ft/day value calculated by the previous method. All values used in both methods are provided in more detail in Section 8.0.

From Equation 5, the velocity of the arsenic will equal

$$V_{As} = \frac{V_w}{R} = \frac{3}{161} = 0.02 \text{ ft/day}$$

That is for an arsenic molecule to travel from the middle of the pond to the down gradient edge of the pond (about 2400 feet) would take about 300 years. This value is based on steady state conditions once the ground water mound is established (See Section 8).

This approach points out the problem of depending entirely upon batch shaker tests to determine distribution coefficients. Essentially in a batch test, a maximum contact between the soil and water is achieved resulting in a maximum K_d value. This should be compared to the column tests which may be more representative of field conditions. In the column experiments, the contact between the soil and water is not as complete and the effective distribution coefficient may be lower.

For example in column X (Figure 6), the arsenic concentrations peak was observed at 60 pore volumes. Based on a hydraulic conductivity of 3 ft/day and an effective porosity of 0.2, 15 pore volumes of fluid would pass through each cubic foot of aquifer material per day. Given this value and the results of the column experiments, the arsenic would be transported rapidly through the aquifer material.



PHASE II FIELD SAMPLING

6.1 SAMPLING PLAN

The batch shaker and sorption tests in conjunction with the column experiments indicate that degradation of groundwater with respect to arsenic will occur if the surface water is allowed to react with soils with arsenic concentrations above 15 ug/g. The objective of Phase II was to define the 15 ug/g contour in order to determine the spatial extent of the duck pond impoundment.

The number of samples required to statistically define concentrations of arsenic at the 95 percent confidence level for the 6 to 12-inch and 12 to 18-inch soil horizons has been calculated to be 42. This number is based on the arsenic values reported from a pilot study (Montana State Division of Health and Environmental Sciences, unpublished) and Equation 6, below (Mason, 1983),

$$n = \frac{t_L^2}{P^2} (CV)^2 \quad \text{--- (6)}$$

where,

- n = the number of samples required
- t_L = the two tailed t-value obtained from the standard statistical tables at the desired level of significance and n-1 degrees of freedom
- P = the allowable margin of error
- CV = the coefficient of variance.

Mason (1983) recommends that P is set at 20 percent, CV at 65 percent and that a 95 percent level of confidence is selected ($t=2.0$ as a first approximation). The use of these values results in an n of 42.

The grid and the soil arsenic concentrations at each node are shown in Figures 8 and 9. The location of the sites maximized the probability that any potential anisotropy in soil arsenic concentrations could be detected.





Figure 8. Soil arsenic concentrations ($\mu\text{g/g}$) in the 6-12 inch layer. The site number is inside the circle.



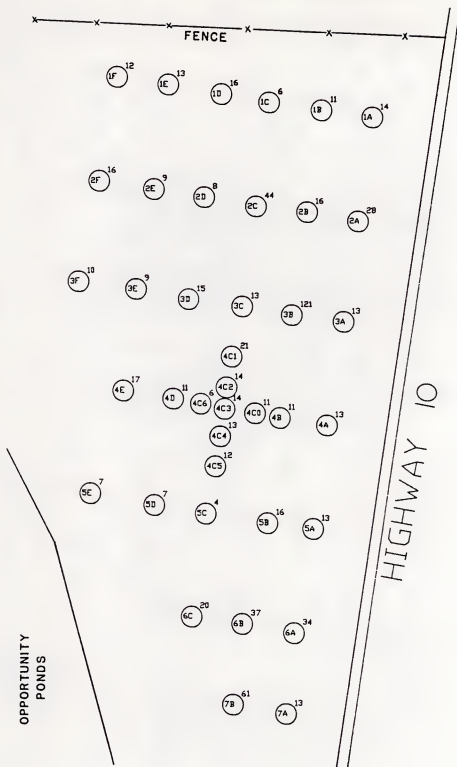


Figure 9. Soil arsenic concentrations (ug/g) in the 12-18 inch layer.
The site number is inside the circle.



This provided 34 sites with a spacing of 1000 feet in a north/south direction and 500 feet in an east/west direction. Six additional sites were selected at 250 foot intervals around node 4 to allow for better evaluation of the range at which the arsenic concentrations are statistically interdependent. The other two samples were duplicates collected at sites 3C and 6B to give a total of 42 samples.

To maximize the probability that representative samples were collected at each node, soil was taken from each corner and in the center of a ten foot square. These five subsamples were composited to yield one sample from which approximately 20 percent (1 Kg) was taken for chemical analysis.

6.2 SAMPLING PROTOCOL

The top five inches of soil was removed and discarded using a clean 4-in. diameter stainless steel auger. A clean 4-in. diameter, 12-in. long piece of PVC pipe was placed in the hole and a clean 3-in. diameter stainless steel auger inserted into the pipe. The next inch of material was removed and discarded to prevent cross-contamination from the top six inches. The next six inches was collected and put on a clean 4-ft by 3-ft piece of polyethylene. This procedure was repeated for all five holes at each site. The five, 6 to 12-inch samples were composited by rolling the soils diagonally from opposing corners of the sheet. A subsample was collected and stored in a ziploc plastic bag.

The PVC pipe was removed and the 6 to 12-inch layer reamed out using the 4-in. auger. The PVC pipe was re-inserted into the hole and the decontaminated 3-in. diameter auger used to remove loose material in the bottom of the hole. The 12 to 18-inch depth was then collected, composited and subsampled on a fresh plastic sheet. Samples from the 6 to 12-inch, 12 to 18-inch, four sample splits, and a decontamination water blank were submitted to the laboratory within three days of collection. Appendix H shows depth measured in some of the holes to assess sampling intervals accuracy.



6.3 KRIGING THE ARSENIC SOIL DATA

Results from the Phase II soil survey (Table 2) indicate that arsenic concentrations in most of the 6 to 12-inch soil layer are above 15 ug/g. Excluding areas south of transect lines R6 and R7 (Figure 8), together with the elevated outlayer concentrations found at sites 2C and 3B, the 6 to 12-inch horizon contains a mean arsenic concentration of 36 ug/g (standard deviation = 24, n = 32). Because of the high average arsenic concentrations, this layer should not be considered as a substrate for the duck ponds.

In the 12 to 18-inch layer, the average arsenic concentration (omitting the hot spots at 2C and 3B and south of transects R6 and R7) is 12.5 ug/g (standard deviation = 4.7, n = 32). This horizon appears to be a viable duck pond substrate.

Semi-variograms were calculated for the 12 to 18-inch soil arsenic data. A spherical model was found to best fit the data assuming an isotropic arsenic distribution. The variogram indicates that the range up to which two points are related is 1,200 feet (Figure 10). Therefore, the spatial intervals chosen for the sampling grid (1,000 feet N/S and 500 feet E/W) are within the limits required for statistical interpolation of contours between sampling points.

Figure 11 shows the Kriged contour map for soil arsenic, predicted when the spherical model is applied to the soil arsenic concentrations. The hot spot in the eastern area is the result of a high arsenic concentration at sites 2C and 3B. If the soil at these sites is excavated to a greater depth than 18 inches, it is likely that the concentrations shown in Figure 12 will apply to the 12 to 18-inch layer.



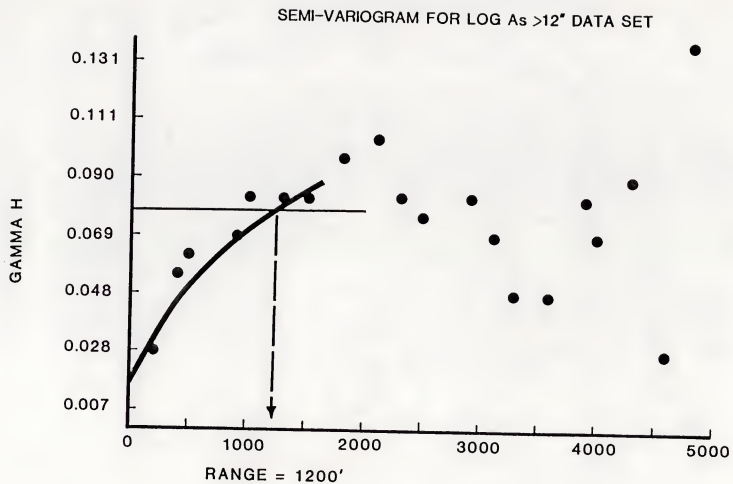


Figure 10. Semi-variogram for arsenic in the 12-18 inch soil horizon.



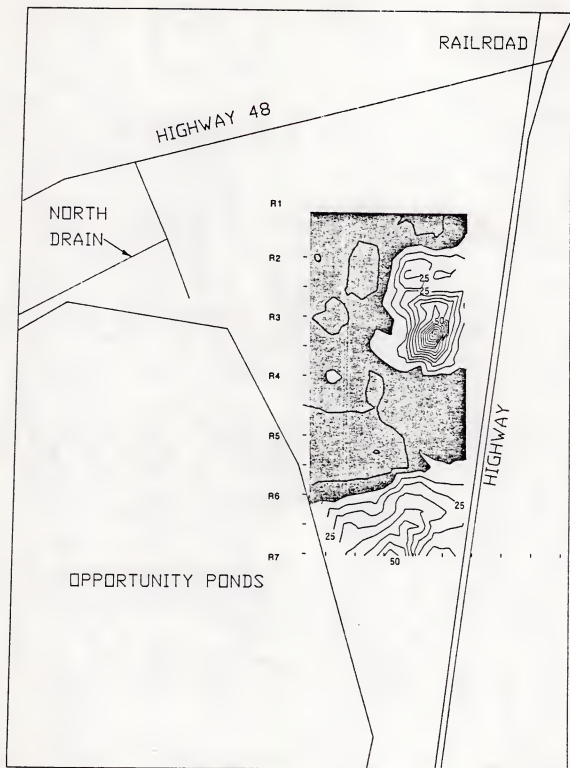


Figure 11. Kriged arsenic map for the 12-18 inch soil horizon. Contours plotted at 5 ug/g intervals. The shaded area represents soil arsenic concentrations less than 15 ug/g.



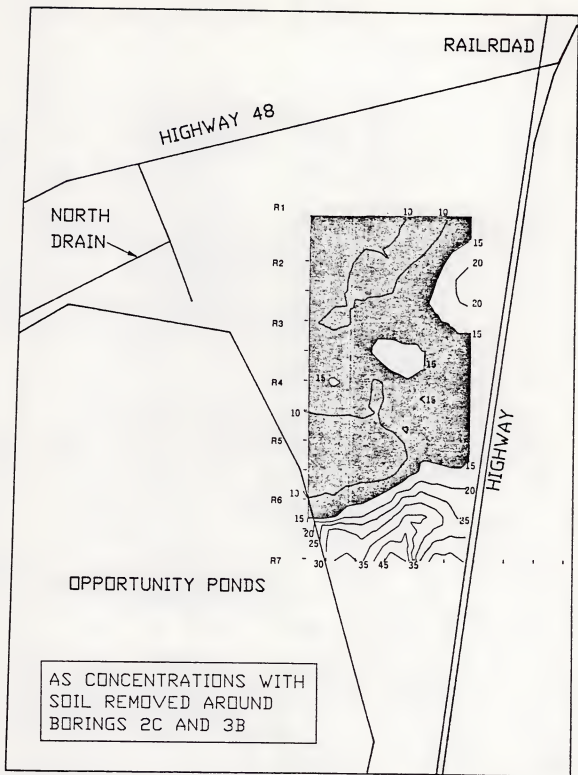


Figure 12. Kriged arsenic map for the 12-18 inch soil horizon excluding sites 3B and 2C. Contours plotted at 5 ug/g intervals. The shaded area represents soil arsenic concentrations less than 15 ug/g.



7.0 SOIL/WATER INTERACTIONS, A GEOCHEMICAL EVALUATION

7.1 X-RAY DIFFRACTION ANALYSIS OF SURFICIAL SOILS

Three samples were submitted for mineralogic analysis. The samples submitted were from the 0 to 6-inch, 12 to 18-inch, and 6 to 18-inch soil horizons from Pit 3C. The results are shown in Table 3. The major feature is the presence of a significant calcium carbonate fraction throughout the profile. In addition, gypsum and dolomite are present in the deeper (6-18 in.) layers.

7.2 WHOLE WATER ANALYSES OF COLUMN LEACHATES

Selected samples of column effluent were submitted for anion and RAS metals analysis. The concentrations of some of the important elements are shown in Table 4. Some general conclusions can be drawn from the data. In all columns, Ca, Mg, and SO_4 are consistently elevated in the initial pore volumes, while higher bicarbonate (HCO_3) concentrations occur only in column A. This suggests that gypsum and possibly dolomite are dissolving in the influent. This hypothesis can be verified by using the geochemical computer code MINTEQ (Pelmy et al. 1984) to calculate the saturation indices of these minerals.

7.3 MODELING THE SOIL/WATER INTERACTIONS

Modeling the system using a thermodynamic equilibrium model is necessary to define potential sinks for the leached arsenic. One process which may attenuate the metal is the precipitation of a calcium arsenate solid phase. This is dependent upon the availability of calcium through the dissolution of calciferous minerals such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcite (CaCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$) known to be present in the soil (Table 3). This mineral suite is undersaturated with respect to the influent mix used in



TABLE 3
MINERALOGIC ANALYSIS (PERCENTAGES) OF SELECTED
SOILS FROM PIT 3C

Mineral	Sample Depth (inches)		
	0-6	6-18	12-18
Quartz	45	34	37
K-spar	9	7	7
Plagioclase	12	8	13
Calcite	17	14	9
Dolomite	tr	4	5
Pyrite/Marcasite	tr	-	-
Gypsum	-	2	5
Amphiboles (mainly Hornblende)	7	5	6
Total Clay	9	26	18
TOTAL	99	100	100

tr = trace amount (<1%)
- = not detected



TABLE 4

ANIONS AND CATIONS IN COLUMN EFFLUENT FROM SELECTED PORE VOLUMES (mg/L)

Number of Pore Volumes	Ca	Mg	Na	K	Al	Fe	SO ₄	HCO ₃	TOC	As
Column A										
1	484	1210	362	39	1.8	0.64	5734	240	282	0.01
2.6	432	225	51	56	0.2	0.26	1290	432	305	0.017
14.6**	127	57	13	47	0.1	0.37	150	296	146	0.49
23.2*	121	49	12	22	0.1	0.42	95	320	145	0.16
29.3	160	45	12	11	0.2	0.35	<5	388	192	0.19
Column D										
0.8	446	560	156	108	<0.4	0.51	3856	80	93	0.02
2.2	466	344	168	107	<0.04	0.18	2467	100	45	0.016
6.8	189	79	10	<0.5	<0.1	8.2	1625	142	61	0.071
Column X										
1	344	1030	311	28	<0.4	<0.25	5864	72	78	0.011
4.5	364	144	17	28	<0.04	0.09	1461	100	39	0.007
28*	115	17	12	6	0.08	0.18	195	144	51	0.003
51*	96	21	12	4.6	0.04	0.14	220	136	47	0.019
Column Z										
1	581	148	28	93	<0.4	<0.25	1959	60	67	0.38
5.7	389	30	99	35	0.15	0.2	852	112	47	0.9
11.7	125	9	11	57	0.3	2.5	193	168	63	2.72
Mix	112	21	13	2.4	0.1	0.15	117	124	45	<0.01
Blank	<0.4	<0.01	<0.9	<0.5	<0.04	0.2	<5	<5	<5	<0.01

* Indicates apparent equilibrium reached with respect to the effluent arsenic concentration.

** Indicates maximum arsenic concentration in column effluent.



all the experiments, indicating that these minerals can dissolve into solution. Appendix I lists the input file and output data from the MINTEQ simulations.

Table 5 shows the predicted concentrations of Ca, Mg, and SO_4 assuming that gypsum, calcite, and dolomite reach equilibrium with an influent mix water at a pH of 6.9. Agreement between the predicted metal concentration and the effluent concentrations of these analytes from Column A (Table 4) is excellent. This suggests that the mineral suite reaches equilibrium with the solution after the passage of approximately two pore volumes of fluid. At this point, sufficient gypsum and dolomite have dissolved that the source becomes exhausted and the concentrations subsequently decrease. The significance of this observation is that at equilibrium $\text{Ca}(\text{AsO}_4) \cdot 6\text{H}_2\text{O}$ is still undersaturated by nine orders of magnitude and is, therefore, not anticipated to precipitate. This approach must be used because the form of arsenic in the soil is not known, hence cannot be incorporated into the mineral suite used in MINTEQ. It is likely that the dissolution of carbonates at a pH of 8.0 in the interstitial water (as in the column tests) will result in a 50 percent attenuation of H_2AsO_4^- or HAsO_4^{2-} onto any clay or limonitic substrates present in the soil profile (Goldberg 1986). This is in good agreement with the result of the sorption test described in this document (Figure 4).

The valence state of the arsenic can be determined using the approach of Petersen and Carpenter (1986) who described the distribution of arsenic in sediment interstitial waters using the equation:

$$\log \frac{\text{As(III)}}{\text{As(V)}} = -(2 * \text{pE}) - 6.46 \quad \text{--- (7)}$$

$$\text{where } \text{pE} = \frac{\text{Eh(volts)}}{0.0596}$$



TABLE 5
COMPARISON OF COLUMN A EFFLUENT
WITH DIFFERENT MINTEQ SIMULATIONS (mg/L)

Parameter	Influent Mix	Effluent from Column A Pore Volume 2.6	MINTEQ Simulation		
			Gypsum	Dolomite Gypsum	Gypsum Dolomite Calcite
Ca	112	430	432	512	396
Mg	20.5	225	20.5	74	224
HCO ₃	120	432	120	291	2
SO ₄	117	1290	117	864	1342



At a pH of 7.3, As(III) constitutes one percent of the total arsenic at an Eh of -100 mV. Extrapolating this equation to the Anaconda sewage lagoons indicates that the majority of the arsenic will be in the +5 oxidation state, even at the lower Eh values measured in column A effluent, making it a candidate for the sorption phenomenon already described.

The conclusion from the geochemical modeling is that there will be rapid dissolution of gypsum and dolomite together with concomitant calcite precipitation.



8.0 ANALYSIS OF DILUTION OF VERTICALLY MIGRATING LEACHATE BY GROUND WATER

The objective of this section is to estimate the extent of mixing between the vertically migrating, arsenic rich solution, and the laterally moving ground water.

8.1 APPROACH AND ASSUMPTION

A simplified approach using a control volume and mass balance concept was used. The following assumptions were made:

- o The duck pond size is 2,640 ft by 4,750 ft (area = 1.25×10^7 ft²).
- o The average thickness of the unsaturated zone in the area of the proposed pond is 7.3 ft. However, the maximum mound height due to infiltration is set at 5.5 ft to allow for seasonal variations in the height of the water table.
- o C_p is the arsenic concentration of seepage from the pond. This value was estimated for these calculations to be 180 ug/L from column test A which had an arsenic concentration of 16 ug/g in the top layer of soil.
- o C_a is the arsenic concentration in the aquifer. This value is based on ground water samples taken near the area and appears to be 4 ug/L.
- o The specific yield of the aquifer is 0.20.
- o The initial saturated thickness of the shallow alluvial aquifer is 25 ft, with K_h (horizontal hydraulic conductivity) estimated between 50 and 200 ft/day, and with a regional gradient (I) of 0.01 (Tetra Tech 1985). The aquifer is underlain by impermeable strata.
- o The pond water mixes with the top 5 ft of the aquifer within approximately one mile downgradient of the center of the pond (based on flow net estimates).
- o The system has reached equilibrium; i.e., steady state conditions were considered.
- o The hydraulic conductivity of the aquifer will not be altered by dissolution or precipitation of carbonate or sulfate minerals.



Using an estimated hydraulic conductivity of 50 ft/day, the seepage from the pond can be calculated as below.

8.2 INFILTRATION FROM POND

The maximum mound height of 5.5 ft corresponds to an infiltration of 24,830 cubic feet per day (cf/d). This estimate was based on the artificial recharge model by Molden, Sunada and Varner (Colorado State University, 1984), using the input parameters given in the assumptions above. This model is based on the radial flow solution of ground water mound development and uniform percolation presented by Hantush.

8.3 AQUIFER DISCHARGE

It was estimated that only the top 5 ft of the aquifer will mix with the pond seepage. This is based on flow net estimates and does not incorporate dispersion. The aquifer cross-section available for dilution of seepage from the pond was estimated to be approximately 35,000 ft². The aquifer discharge that will mix with the pond seepage is then estimated as Q_a, where $Q_a = KhIA = (50 \text{ ft/d}) * (0.01) * (35,000 \text{ ft}) = 17,500 \text{ cf/d}$.

8.4 CONCENTRATION

To compute the resulting concentration of arsenic in the aquifer, the mass balance equation is used, as given below:

$$(Q_a) * (C_a) + (Q_p) * (C_p) = (Q_t) * (C_t)$$

where Q_a = aquifer flow
Q_p = pond infiltration
Q_t = Q_a + Q_p
C_a = concentration of arsenic in ground water aquifer
C_p = concentration of arsenic in pond seepage
C_t = concentration of mixed water



$$\begin{aligned}
 \text{then } C_t &= \frac{Q_a * C_a + Q_p * C_p}{Q_t} \\
 &= \frac{(17,500 \text{ cf/d})(4 \text{ ug/L}) + (24,830 \text{ cf/d})(180 \text{ ug/L})}{42,330 \text{ cf/d}} \\
 &= 110 \text{ ug/L}
 \end{aligned}$$

Therefore, the dilution is approximately 40 percent.

8.5 CONCLUSIONS

A preliminary estimate of the effect of installing duck ponds on the water quality of the alluvial aquifer has been made. These calculations indicate that the maximum amount of pond inflow into the aquifer is approximately 25,000 cf/d (based on a hydraulic conductivity of 50 ft/d). If 1 MGD of wastewater/North Ditch water (133,690 cf/d) is applied to the pond, then the remainder (108,700 cf/d), or 0.8 MGD will flow directly from the pond into the stream. In addition, based on the mounding calculations, discharge to the stream from the ground water aquifer is estimated to be approximately 0.1 MGD (13,000 cf/d).

The above calculations demonstrate that if the seepage from the duck ponds mixes with the top five feet of the underlying aquifer, the resultant arsenic concentration in the upper five feet of the aquifer would be diluted approximately 40%. This maximum dilution is at a distance of approximately one mile downgradient from the center of the pond. The calculations and uncertainties need to be evaluated, as listed below:

1. How much mixing will occur between the mounded water and the aquifer, and at what distance downgradient of the pond will complete mixing be achieved?
2. Will the arsenic concentration in the ground water influx remain at 4 ug/L or will it increase with time?
3. How will the ground water flow regime of the site be affected by other remedial actions in the area?



4. Where are the potential receptors located, and at what points or in which areas can degradation of ground water quality be tolerated?
5. Will the aquifer porosity change as a result of the precipitation or dissolution of carbonates or sulfates?
6. How will ground water discharge to adjacent streams influence the flow regime and degree of mixing?
7. Do distinct flow channels exist in the aquifer?

Item 1 is probably the most complex of the above questions. The point at which complete mixing is achieved will be dependent upon:

- o The rate of sewage inflow to the duck ponds.
- o The size of the pond(s).
- o Dispersivity characteristics of the aquifer.
- o Vertical hydraulic conductivity and vertical gradients in the aquifer.
- o Variations in aquifer thickness and/or interconnection with deeper alluvial strata.

Overall, the hydrologic evaluation indicates that the ground water mound from the duck pond will be quite extensive and that mixing of the infiltrating pond water with the ground water will be limited to the upper zone of the aquifer. For example, at the downgradient corner of the pond, the following "layers" of water will be present (from the surface to bottom of the aquifer):

- o A mound of pond water "on top of" the ground water. The mound at the downgradient corner of the pond will be approximately 4 feet in height and will have an arsenic concentration equal to the leachate concentration. That is, this mound of water will experience no dilution from the ground water aquifer. If the leachate concentration from the pond is limited to 50 ug/L of arsenic, then a monitor well in the upper 4 feet of water will show a concentration of arsenic of 50 ug/L.
- o A mixed zone of pond water and ground water. This zone is estimated to be about 1.25 feet thick at the edge of the pond and



is the upper 1.25 feet of the pre-existing ground water aquifer. The concentration of arsenic in this zone will be a combination of both ground water and pond water leachate. Previously calculations indicate that ultimately the arsenic concentration of the leachate will be diluted 40 percent further downgradient. At the edge of the pond the dilution may be only 15 percent. If a monitoring well were placed in this 1.25 foot zone and the arsenic in the leachate from the pond was limited to 50 ug/L, the resulting water quality in the zone would be about 40 ug/L.

- o A lower zone of ground water. Essentially this zone is not impacted by the infiltration from the duck ponds. A monitoring well in this zone should show background concentrations of arsenic.

If this type of model is correct, the ground water recharge to the stream would be composed mostly of the upper zones of undiluted mound water and mixed water. That is, the undiluted mound water will discharge to Mill Creek having arsenic concentrations similar to the leached interstitial water arsenic concentrations. The data currently available are sufficient to conduct this preliminary feasibility assessment only. If better quantification is necessary, we recommend that a pilot study be undertaken to resolve the uncertainties. We also recommend that specific design constraints be identified in terms of (1) acceptable ground water quality at specific locations, and (2) critical areas where ground water quality must meet standards for arsenic.



9.0 FIELD VERIFICATION OF THIS WORK

If the decision is made to proceed with development of the duck ponds, it will be important to verify that ground water is not being degraded by arsenic leached from the soils.

This may be accomplished through the use of monitoring wells for ground water, lysimeters for the initially unsaturated alluvial material, and "pore water peepers" for the substrate material. During removal of the surficial soil, ongoing arsenic analyses must be conducted to ensure that elevated soil arsenic concentrations (above 15 ug/g) are removed.

If arsenic is detected in the ground water, it would be informative to determine the oxidation state. If aqueous arsenic existed in the +3 state, remedial action may be necessary to retard the mobility of the neutral H_3AsO_3^0 ion. Arsenic in the +5 state will be less mobile because the arsenic form will sorb more strongly to available sites the substrate as has been demonstrated by the sorption experiment in this study.



10.0 CONCLUSIONS

The major conclusions drawn from the duck ponds evaluation are:

1. A soil arsenic concentration of 15 ug/g is likely to result in the generation of a leachate bearing 50 ug/L of arsenic at equilibrium.
2. At least the top 12 inches of soil must be removed from the area to be submerged in order to prevent significant degradation of the ground water.
3. In selected locations in the vicinity of sites 2C and 3B, soil may have to be removed to a depth of 18 inches in order to prevent ground water degradation.
4. An area to the south of transect R5 appears unsuitable for any impoundment based on elevated soil arsenic concentrations in both the 6- to 12-inch and 12- to 18-inch layers.
5. Calculations indicate that the leachate percolating through the unsaturated zone following impoundment will be diluted by, at most, 40 percent by the upper five feet of the laterally migrating ground water. However, an upper zone will exist in which no dilution will occur.
6. Installation of the impoundments should be accompanied by analysis of soil arsenic levels and followed by monitoring of ground water and interstitial water to determine the rates, if any, of arsenic release.



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APPENDIX A

SHAKE EXTRACTION OF SOLID WASTE WITH WATER










Designation: D 3987 - 81

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Standard Test Method for SHAKE EXTRACTION OF SOLID WASTE WITH WATER¹

This standard is issued under the fixed designation D 3987; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal.

1. Scope

1.1 This method covers a procedure for leaching of solid waste to obtain an aqueous solution to be used to determine the materials leached under the specified testing conditions.

1.2 It provides for the shaking of a known weight of waste with water of specified composition and the separation of the aqueous phase for analysis.

2. Applicable Documents

2.1 ASTM Standards:

- D 75 Sampling Aggregates²
- D 420 Recommended Practice for Investigating and Sampling of Soil and Rock for Engineering Purposes³
- D 1129 Definitions of Terms Relating to Water³
- D 1193 Specification for Reagent Water³
- D 1888 Tests for Particulate and Dissolved Matter in Water³
- D 2216 Laboratory Determination of Moisture Content of Soils³
- D 2777 Practice for Determination of Precision and Bias of Methods of Committee D-19 on Water³
- D 2234 Collection of a Gross Sample of Coal⁴
- D 3370 Practices for Sampling Water³
- E 122 Recommended Practice for Choice of Sample Size to Estimate the Average Quality of a Lot or Process⁵

3. Significance and Use

3.1 This method is intended as a rapid means for obtaining an extract of solid waste. The extract may be used to estimate the release of certain constituents of the solid waste under

the laboratory conditions described in this procedure.

3.2 This method is not intended to provide an extract that is representative of the actual leachate produced from a solid waste in the field or to produce extracts to be used as the sole basis of engineering design.

3.3 This method is not intended to simulate site-specific leaching conditions. It has not been demonstrated to simulate actual disposal site leaching conditions.

3.4 It is intended that the final pH of the extract reflect the interaction of the extractant with the buffering capacity of the solid waste.

3.5 It is intended that the water extraction simulate conditions where the solid waste is the dominant factor in determining the pH of the extract.

3.6 The method produces an extract that is amenable to the determination of both major and minor constituents. When minor constituents are being determined, it is especially important that precautions are taken in sample storage and handling to avoid possible contamination of the samples.

3.7 This method has been tested to determine its applicability to certain inorganic components in the solid waste (see Appendix X1). The method has not been tested for applicabil-

¹ This method is under the jurisdiction of Committee D-34 on Waste Disposal and is the direct responsibility of Subcommittee D 34.02 on Extraction and Leachate Testing. Current edition approved March 26, 1981. Published June 1981.

² Annual Book of ASTM Standards, Part 19.

³ Annual Book of ASTM Standards, Part 31.

⁴ Annual Book of ASTM Standards, Part 26.

⁵ Annual Book of ASTM Standards, Parts 15 and 41.



ity to organic substances and volatile matter (see 5.3).

3.8 The agitation technique and rate and the liquid-to-solid ratio specified in the procedure may not be suitable for extracting all types of solid waste. (See discussion in Appendix X2.)

4. Definitions

4.1 For definitions of terms used in this method, see Definitions D 1129.

5. Apparatus

5.1 *Agitation Equipment*—Agitation equipment of any type that will produce constant movement of the aqueous phase equivalent to that of a reciprocating platform shaker operated at 60 to 70 1-in. (25-mm) cycles per minute without incorporation of air is suitable. A cycle shall be understood to include one forward and one equal return movement. Equipment used shall be designed for continuous operation without heating the samples being agitated (see discussion of agitation in Appendix X2).

5.2 *Membrane Filter Assembly*—A borosilicate glass or stainless steel funnel with a flat, fritted base of the same material and membrane filters.

5.3 *Containers*—Round, wide-mouth bottles of composition suitable to the nature of the solid waste and the analyses to be performed, and constructed of materials that will not allow sorption of constituents of interest. One-gallon (or 4-litre) bottles should be used with 700-g samples and ½-gal (or 2-L) bottles with 350-g samples. Multiples of these sizes may be used for larger samples. These sizes were selected to establish suitable geometry and provide that the sample plus liquid would occupy approximately 80 to 90 % of the container. Bottles must have a watertight closure. Containers for samples where gases may be released should be provided with a venting mechanism. (Note that the venting of the container has the potential to affect the concentration of volatile extracts in the extract.) Containers should be cleaned in a manner consistent with the analyses to be performed.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the

American Chemical Society, where such specifications are available.¹ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type IV reagent water at 18 to 27°C (Specification D 1193).

7. Sampling

7.1 Obtain a representative sample of the solid waste to be tested using ASTM sample methods developed for the specific industry where available.

7.2 Where no specific methods are available, sampling methodology for materials of similar physical form shall be used.

7.3 A minimum sample of 5000 g shall be sent to the laboratory (see Method E 122).

7.4 It is important that the sample of the solid waste be representative with respect to surface area, as variations in surface area would directly affect the leaching characteristics of the sample. Solid waste samples should contain a representative distribution of particles sizes.

7.5 Keep samples in closed containers appropriate to the sample type prior to the extraction in order to prevent sample contamination or constituent loss. Where it is desired to extract biologically or chemically active samples in their existing state, store the samples at 4°C (Practices D 3370) and start the extraction within 8 h. Where it is desired to extract such samples in a state representative of the results of biological or chemical activities, the samples may be specifically handled to simulate such activities. Record the storage conditions and handling procedures in the report.

8. Sample Preparation

8.1 For free-flowing particulate solid wastes, obtain a sample of the approximate size required in the test by quartering the sample (Section 7) received for testing on an impermeable sheet of glazed paper, oil cloth, or other

¹ "Reagent Chemicals, American Chemical Society Specifications," *Am. Chemical Soc., Washington, D. C.* For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph E. H. Van Nostrand Co., Inc., New York, N. Y., and the "United States Pharmacopoeia."



flexible material as follows:

8.1.1 Empty the sample container into the center of the sheet.

8.1.2 Flatten out the sample gently with a suitable straightedge until it is spread uniformly to a depth at least twice the maximum particle diameter particle size.

8.1.3 Remix the sample by lifting a corner of the sheet and drawing it across, low down, to the opposite corner in a manner that the material is made to roll over and over and does not merely slide along. Continue operation with each corner, proceeding in a clockwise direction. Repeat this operation ten times.

8.1.4 Lift all four corners of the sheet towards the center and holding all four corners together, raise the entire sheet into the air to form a pocket for the sample.

8.1.5 Repeat Step 8.1.2.

8.1.6 With a straightedge at least as long as the flattened mound of sample (such as a thin-edged yard stick), gently divide the sample into quarters. An effort should be made to avoid using pressure on the straightedge sufficient to cause damage to the particles.

8.1.7 Discard alternate quarters.

8.1.8 If further reduction of sample size is necessary, repeat Steps 8.1.3 through 8.1.7. A minimum sample size of 350 g is recommended for each extraction. Additional samples should be provided for determination of solids content. If smaller samples are used in the test, report this fact.

8.2 For field-cored solid wastes or castings produced in the laboratory, cut a representative section weighing approximately 350 or 700 g for testing, plus samples for determination of solids content. Shape the sample so that the leaching solution will cover the material to be tested.

8.3 For fluid solid wastes, mix thoroughly in a manner that does not incorporate air to assure uniformity before withdrawing a 350 or 700-g sample for test. Take samples for determination of solids content at the same time as the test sample.

9. Procedure

9.1 Record the physical description of the sample to be tested including particle size so far as it is known.

9.2 *Solids Content*—Determine the solids content of separate portions of the sample as

follows:

9.2.1 Dry to constant weight two dishes or pans of size suitable to the solid waste being tested at $104 \pm 2^\circ\text{C}$. Cool in a desiccator and weigh. Record the value to ± 0.1 g.

9.2.2 Put an appropriately sized portion of sample of the solid waste to be tested into each pan. Scale the weight used to the physical form of the solid waste tested. Use a minimum of 50 g but use larger samples where particles larger than 10-mm in average diameter are being tested. Weigh. Record the weight to ± 0.1 g.

9.2.3 Dry 16 to 20 h at $104 \pm 2^\circ\text{C}$. Certain solid wastes, such as scrubber sludges, may contain compounds that are subject to calcination at the specified drying temperature. Dry these compounds at lower temperatures. For example, gypsum may be successfully dried at 45°C (Method C 471) and $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ wastes at 85°C . Record the actual temperature and time of the drying period.

9.2.4 Cool to room temperature in a desiccator and reweigh. Record the weight to ± 0.1 g.

9.3 *Shake Procedure*—Weigh or tare the container to be used in the shake test to the nearest or within 1 g.

9.4 Add the container approximately 700 g of solid waste (Section 8) and determine and record the weight of sample used to 1 g. If weights other than 700 g are used, note in the report.

9.5 Add to the container a volume of test water (6.2) equal in milliliters to four times the weight in grams of the sample used in 9.4. See discussion of dilution ratio in Appendix X2.

9.6 Close the container. Invert the container approximately 25 times per minute for 3 min. Place the container upright on the agitation equipment.

9.7 Agitate continuously for 48 h ± 0.5 h at 18 to 27°C .

9.8 Open the container. Observe and record any physical changes in the sample and leaching solution.

9.9 Shake the container to mix the entire sample thoroughly. Let the sample settle for 5 min; then separate the bulk of the aqueous phase from solid phase by decantation, centrifugation, or filtration through filter paper as appropriate. Then vacuum or pressure filter the liquid through a $0.45\text{-}\mu\text{m}$ filter. If these separation means result in prolonged filtering time,



a 8- μ m filter or other device may be used. Record any such deviations in the report.

9.10 The filtrate obtained in 9.9 is the extract mentioned elsewhere in this method. Measure the pH of the extract immediately, then preserve the extract in a manner consistent with the chemical analysis or biological testing procedures to be performed (Practices D 3370). If sufficient liquid phase is not available for the analyses, so indicate in the report and do not continue the procedure; or alternatively, perform the extraction procedure on additional samples of the solid waste to obtain sufficient liquid phase. Where phase separation occurs during the storage of the extract, appropriate mixing should be used to ensure the homogeneity of the extract prior to its use in such analysis or testing.

9.11 Analyze the extract for specific constituents or properties or use the extract for biological testing procedures as desired using appropriate ASTM standard methods. Where no appropriate ASTM methods exist, other methods may be used and recorded in the report.

10. Calculation

10.1 Calculate the solids content of the individual samples from the data obtained in 9.2 as follows:

$$S = A/B$$

where:

A = weight in grams of sample after drying,

B = original weight in grams of sample, and

S = solid content, g/g.

Average the two values obtained. Record as the solids content.

11. Report

11.1 The report shall include the following:

11.1.1 Source of the solid waste, date of

sampling, and sample preservation used.

11.1.2 Description of the solid waste including physical characteristics and particle size, if known (9.1).

11.1.3 Solids content (9.2).

11.1.4 Sample weight if other than 700 g.

11.1.5 Drying time and temperature if other than 16 to 20 h at $104 \pm 2^\circ\text{C}$.

11.1.6 pH and results of specific analyses calculated in appropriate units. State analytical procedures used, and filter used if other than 0.45 μm .

11.1.7 Observation of changes in test material or leaching solution recorded in 9.8.

11.1.8 Date leach testing started, preservation used for extract, and date of analysis.

12. Precision and Accuracy

12.1 No information is presently available as to the precision or accuracy of the analysis of specific constituents in the extract. It is recommended that users of this test validate the applicability of their chosen methods of detection by spiking portions of the extract, before using these methods for the analysis of the extract.

12.2 Based on a collaborative series of tests on six solid wastes including fly ash, scrubber sludge, API separator sludge, metal finishing waste, textile waste, and soil, the precision of iron and calcium determinations for these specific solid wastes was measured. Information on the test program is provided in Appendix XI.

12.3 The precision of this method may vary depending on the solid waste being tested and on the element being extracted.

12.4 Determination of the accuracy of this method is not possible, as no standard reference material exists.



APPENDICES

XI. COLLABORATIVE TEST PROGRAM

X1.1 Based on a collaborative series of tests on six solid wastes including fly ash, scrubber sludge, API separator sludge, metal finishing waste, textile waste, and soil, the precision of this method for these specific materials, including variability of the extraction test and the analytical procedure, may be expressed as shown below. Twenty one laboratories participated in the collaborative test program, and each of the six solid wastes was tested by at least five of the laboratories, with a single operator performing three extraction replicates. The collaborative test program was conducted with both an unclear definition of whether a stroke constituted forward-return movement (see 5.1) and without the inversion instruction (see 9.6). It has not been determined how this contributed to the observed deviation.

X1.1.1 For calcium in concentrations ranging between 2.8 and 220 mg/L:

$$S_x = 0.311X + 9.26$$

$$S_x = 0.192X - 1.59$$

where:

S_x = overall precision,

S_x = single-operator precision, and

X = determined concentration of Ca, mg/L.

X1.1.2 For iron, in concentrations ranging from 0.06 and 1.4 mg/L:

$$S_x = 0.792X - 0.013$$

$$S_x = 0.543X - 0.023$$

where:

S_x = overall precision,

S_x = single-operator precision, and

X = determined concentration of Fe, mg/L.

The collaborative data are on file at ASTM Headquarters, 1910 Race St., Philadelphia, Pa. 19103 and may be obtained on loan by requesting R.R. D 19-1008.

X2. AGITATION TECHNIQUE AND RATE, AND LIQUID/SOLID RATIOS

X2.1 While the major effort relative to development of the test method has been undertaken at the agitation rate and liquid/solid ratios specified in the method, it is recognized that these variables may significantly influence the results on certain solid wastes, and that they may not be adequate for certain solid wastes.

X2.1.1 The possible effects of varying the agitation technique and rate include degree of mixing, rate of release of constituents, and particle abrasion ef-

fects. The precision of the method may also be influenced.

X2.1.2 The possible effects of varying the dilution ratio include degree of mixing, rate of release of constituents (and possible concentration effects, depending on availability), and particle abrasion effects.

X2.2 The agitation techniques and rates and dilution ratios used by other proposed extraction methods differ from those used in this method.

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any device mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1910 Race St., Philadelphia, Pa. 19103, to which it will be referred for further hearing regarding your comments. Failing satisfaction there, you may appeal to the ASTM Board of Directors.



APPENDIX B

LEACH TEST DATA



LEACH TEST DATA

(1) TEST MIX UNDER OXIDIZING CONDITIONS

Soil	Soil Mass (g)	Fluid Volume (mL)	Arsenic (As) (ug/L)	Equivalent Pore Volumes
3C 0-6 inches (150 ug As/g) 150	0.25 2.5 150	250 250 4800	80 650	
3C 6-12 inches (30 ug As/g)	0.25 2.5 12.5 250	250 250 250 250	19 110 310 700	1000 100 20 1.0
3C 12-18 inches (8 ug As/g)	0.25 2.5 250	250 250 250	4.4 11 25	1000 100 1
5C 6-12 inches (4 ug As/g)	0.25 2.5 150	250 250 150	3.9 6.1 8.9	
2B 12-18 inches (16 ug As/g)	0.25 2.5 12.5 50 250	250 250 250 250 250	22 53 130 200 260	

(2) COMPARISON OF OXIC AND ANOXIC CONDITIONS

from Start (hrs)	Soil Mass (g)	Fluid ¹ Volume (mL)	Oxic As (ug/l)	(ug/l)	Anoxic As (ug/l)	(ug/l)
3.5	25	600	13	0.6	16	0.6
7	25	550	9	-	11	2.3
22	25	500	13	-	10	1.3
44	25	450	17	-	14	3.1

¹ 50 mL of fluid extracted at each time step.

The standard deviation of these samples is calculated from at least three replicate analyses of each sample. Based on the standard deviations there is no significant difference between the treatments after 3.5 hours.



APPENDIX C

DRAFT METHOD FOR LEACHING SOLID WASTE IN A COLUMN APPARATUS
UNDER CONSTANT HEAD CONDITIONS



DRAFT METHOD FOR LEACHING SOLID WASTE IN A COLUMN APPARATUS

1. Scope

1.1 This method is a standard laboratory procedure for generating aqueous leachates from waste materials using a column apparatus. Analysis of column effluent can provide information on the liquid/solids ratio or time dependent leaching characteristics of waste under the conditions used in the test.

1.2 It provides for the passage of an aqueous fluid (e.g., distilled water) through materials of known mass in a saturated upflow mode.

1.3 This method is intended to allow the tester to attempt to simulate site specific leaching conditions. The ability of the method to simulate such conditions has not, however, been determined.

2. Applicable Documents

2.1 ASTM Standards

- D-1129 definition of terms relating to water
- D-1193 specification for reagent water
- D-1888 tests for particulate and dissolved matter in water
- D-2216 laboratory determination of moisture content of soils
- D-3370 practices for sampling water
- E-122 recommended practice for choice of sample size to estimate average quality of a lot or process
- D-854 specific gravity of soils
- D-698 moisture-density relations of soils and soil aggregate mixtures using a 5.5 lb hammer and a 12-inch drop
- D-2434 permeability of granular soils (constant head)
- EM1101-2-1906 Army Corps of Engineers falling head permeability test
- D-422 particle size analysis of soils
- D-1293 test for pH of water
- D-1125 test for electrical conductivity and resistivity of water
- D-1498 practice of oxidation-reduction potential of water

3. Terminology

3.1 Several terms used in this practice are defined in ASTM D-1129; other terms are defined below.

3.2 Waste Material - any material, regardless of state of aggregation which will be discarded to the environment.

3.3 Disposal - placement of a material in the environment with the intent of terminating responsibility for it after some finite period of time.



3.4 Pore Volume - the void volume in a bed of granular material existing between the solid particles. Also called the interstitial volume.

4. Significance and Use

4.1 This method is intended to provide an aqueous leaching of a material in a dynamic partitioning manner at the high solid to liquid ratios encountered in landfills.

4.2 This method is not intended to produce results which will be used as the sole basis for (a) the engineering design of a landfill disposal site, or (b) the classification of wastes based on leaching characteristics.

4.3 It is intended that the material used in the procedure be physically, chemically and biologically representative of the form in which it will be landfilled.

4.4 This practice may not be applicable to materials with low permeability which result in excessively long testing periods.

4.5 This method may not be applicable to materials which are physically affected by the ascending mode of operation.

4.6 This method may not be applicable to materials which change physically over time, for instance self-hardening materials.

4.7 This method is not designed to produce a leachate that can be meaningfully characterized with respect to total suspended solids.

4.8 This method is not applicable to the characterization of wastes with regard to the leaching of volatile compounds.

5. Apparatus

5.1 The column can be constructed of acrylic components or of borosilicate glass depending on the nature of the leachate analysis.

5.2 Acrylic Columns

5.2.1 Acrylic components are suitable for generating leachates to be analyzed for inorganic constituents and general indicator parameters such as BOD, COD, TOC, pH, specific conductance, dissolved solids, alkalinity, etc.

5.2.2 The column body is cast acrylic tubing, 12 inches in length with an inside diameter of 4 inches. A cylinder wall of sufficient thickness (~1/4 inch) should be selected with regard to operating pressures. The use of extruded tubing should be avoided because of the potential for increased wall effects due to the longitudinal grooves that may be present.

5.2.3 Endplates are constructed of acrylic sheeting cut to 7 inches by 7 inches. A thickness of 1 inch is required to allow for a machined 1/4-inch deep circular inset to contain the porous flow distribution plate. Both endplates should be drilled and tapped for a 1/4-inch stainless steel tube fitting.

5.2.4 The circular gaskets at both ends of the column should be chemically inert and as thin as possible while still providing a good seal. The gasket diameter should overlap the inside column diameter by 1/8 inch to prevent the gasket from being forced out while under pressure.



5.2.5 Flow distribution disks should be of porous polyethylene with a nominal pore size diameter of 70 microns. The disk thickness should be 1/4 inch with a diameter equal to the inside diameter of the column (4 inches).

5.2.6 The endplates are attached to the cylinder by the means of eight 1/4-inch threaded rods as shown in Figure .

5.2.7 All tubing used with acrylic columns should be 1/4-inch OD polyethylene.

5.2.8 The assembled acrylic column apparatus is shown in Figure .

5.3 Glass Columns

5.3.1 Columns used to generate leachate to be analyzed for specific organic chemicals should be made of borosilicate glass.

5.3.2 Glass columns can be made from commercially available glass pipe generally known as beaded pressure pipe. The pipe is specified by its inside diameter and can be cut and re-beaded to any length.

5.3.3 The endcaps for the glass columns are made from modified commercially available "clean-out" plugs. The modification consists of filling the void space within the cap with a porous flow distribution disk constructed of an inert material. The flow distribution disk should fit snugly in the endcap and be flush with the endcap lip. A thick walled glass tube should be fused through the endcap from the outside to provide a site for the tubing attachment.

5.3.4 The gaskets sealing the endcaps to the cylinder are typically fluorocarbon rings surrounded by a flexible elastomeric sleeve. Pressure is applied by a stainless steel slip ring. The gaskets, sleeves, and slip rings can be ordered as parts of the beaded glass pressure pipe system.

5.3.5 The diffusion disk should be a porous fluorocarbon polymer material with a nominal pore size of 70 microns. The diameter should be equal to the inside diameter of the column endcaps.

5.3.6 Tubing should be 1/4-inch diameter and constructed of or lined with fluorocarbon polymer with stainless steel tube fittings.

5.3.7 The assembled borosilicate glass column is shown in Figure .

5.4 A pressurized reservoir vessel is used to contain the aqueous fluid used to generate leachate. This usually is a column identical to the leaching column with the exception of the diffusion disks which are not required. A port at the top may be helpful during refilling.

5.5 Balance, 10-kg capacity, with a 1-g sensitivity.

5.6 Compressed gas source (prepurified nitrogen or argon) with a two-stage delivery regulator (0-50 psig).



6. Reagents and Materials

6.1 Reagent grade chemicals should be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available. Other grades may be used, provided that it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 Unless otherwise indicated, references to water shall be understood to mean Type IV Reagent Water, specification D-1193.

7. Safety Precautions

7.1 The general operating pressure should not exceed 50 psi for a 4-inch diameter glass or acrylic column.

8. Sampling

8.1 A representative sample of the waste to be tested shall be obtained using ASTM sample methods developed for the specific industry where available.

8.2 Where no specific methods are available, sampling methods for materials of physical form similar to the waste shall be used.

8.3 A minimum sample of 5000 g, or three bed volumes, whichever is larger, shall be sent to the laboratory (see Method E-122) for each column.

8.4 Samples shall be kept in closed containers appropriate to the sample type and otherwise protected if necessary prior to the extraction in order to prevent sample contamination or constituent change or loss. Where it is desired to extract biologically or chemically active samples in their existing state, any sample storage required should be at 4°C (Practice D-3370) and the leaching should be started within 8 hours. Where it is desired to leach such samples in a state representative of the results of biological or chemical activities, the samples may be specifically handled to simulate such activities. Record the storage conditions and handling procedures in the report.

9. Preparation of Apparatus

9.1 The assembled apparatus are shown in Figures and .

9.2 Column preparation procedures are specified in Section 10.2.

9.3 When filling the acrylic column with fine grained material, it may be necessary to secure the bottom endplate to the column with the gasket in place to prevent the waste material from becoming trapped underneath the gasket creating a potential for leakage. By placing a 4-inch ID pipe-riser clamp over the waste column, a temporary anchor point is obtained for two threaded rods as shown in Figure .



10. Procedure

10.1 Preparation of Waste for Leaching

10.1.1 A sample of waste should be prepared in a manner which simulates the state the waste is in or will be in as it undergoes leaching in the field. Preparation of the waste may include such factors as curing, and adjustment of moisture content, and density. For such adjustments, the following procedures can be used where appropriate.

10.1.2 Moisture Content - The moisture content should be adjusted to that expected in the field by dewatering or the addition of water. If drying is required, drying conditions should be selected that are appropriate to the waste and disposal scenario of interest. For most purposes drying temperatures of less than 60 degrees centigrade should be used. Higher temperatures may cause excessive loss of the water of hydration of some substances. If the waste is being disposed of in a very dry state, as for instance flyash might be, it may be appropriate to subject the sample to drying temperatures of greater than 60 degrees centigrade before placement in the column. The moisture content of the waste as it is placed in the column should be determined using ASTM method D-2216 and an appropriate drying temperature. (See note number 5 in ASTM D-2216.)

10.1.3 Density - Density is to be adjusted by vibration or compaction to the anticipated field density. The waste material should be packed in the column so that uniform density is achieved. This can be checked by visual observation of the waste in the transparent column.

10.1.4 Curing - For those materials which undergo physical or chemical changes with time, curing for sufficient duration and under appropriate conditions, depending on the waste to be tested, should be accomplished in the column to produce a physical and chemical state representative of the waste as it undergoes leaching in the field.

10.1.5 Particle Size - The particle size distribution of the waste as placed in the column should be representative of that expected in field placement. The maximum particle diameter should not exceed 1/10 of the inside diameter of the column. Size reduction is not normally recommended as it may alter the leaching characteristics of the waste. A knowledge of the particle size distribution and surface area may be useful in interpreting column leaching results. ASTM Methods D-422 and C-819 may be useful for determining particle size distribution and surface area respectively.

10.2 Column Preparation

10.2.1 Before use, all parts of the test apparatus that will contact the waste material, leaching fluid, or product leachate should be cleaned using methods appropriate to the objectives of the test. If the column leachate is to be analyzed for inorganic substances and/or for general indicator parameters such as BOD, COD, TOC, pH, and specific conductance, the acrylic test apparatus may be cleaned by washing with hot detergent water followed by a tap water rinse, followed by rinsing with a 20 percent (1+4) nitric acid solution followed by three rinses with distilled water. If very low concentrations of these substances in the leachate are of interest, more rigorous washing techniques may be necessary. If the column leachate is to be analyzed for specific organic compounds, the glass



apparatus may be cleaned using the ASTM D-3694 procedure for preparation of sample containers, or by using the sample container cleaning methods outlined in the EPA Handbook for Sampling and Sample Preservation of Water and Wastewater (). The EPA procedure calls for washing with hot detergent water followed by a tap water rinse, followed by three or more rinses with organic-free water, followed by rinsing with interference-free redistilled solvent such as acetone or methylene chloride and drying in organic-free air.

10.2.2 The weight of the dried, cleaned, empty column including endcaps, and other fittings necessary to contain the waste, should be determined. Record the inside diameter and height of that part of the column to be filled with waste (i.e. the column cylinder).

10.2.3. When the material is ready to be placed in the column, it should be in a state which is chemically, physically, and biologically representative of that waste under the field conditions of interest.

10.2.4 Compact or vibrate the waste in five equal layers, by whatever means necessary, to achieve the expected field density, scarifying each layer prior to the placement of a new layer. Take special care to ensure that the material touching the side of the plexiglass column is well compacted in order to prevent seepage of the leaching water between the column and the compacted material. The final height of the compacted material should be equal to the height of the leaching column.

10.2.5 After filling the column, weigh the filled column (including the same fittings as were included when the empty column was weighed).

10.3 Leaching

10.3.1 The leaching process should be conducted in continuous upflow mode.

10.3.2 Saturation - After assembling the column as shown in Figure , the column should be saturated with water by the method outlined in ASTM D-2434 for determining permeability coefficients using a constant head permeameter. In this case, the column assembly replaces the constant head permeameter of that ASTM procedure. If it is determined that it is not possible to saturate the waste using ASTM D-2434, it may be necessary to increase the vacuum used in the procedure and/or attempt to saturate the column under pressure to promote the dissolution of gases.

10.3.3 Water used to saturate the waste should be of the same quality as that to be used to leach the waste in the column. A sample of this water should be collected at the time of saturation and analyzed for the same properties and constituents as will be measured in the column effluent. A sample container will be selected and cleaned and the sample will be collected following the procedures for sampling column effluent.

10.3.4 Determination of Pore Volume - Pore volume is estimated from the measurement of specific gravity of the solids according to ASTM D-854, the mass of the wet solids placed into the column, the moisture content of the material according to ASTM D-2216, and the volume of the column. Although the drying



temperatures used in ASTM D-854 and D-2216 can be selected on the basis of the specific characteristics of the material being dried, the drying temperatures used in the two procedures must be the same for the data to be used for porosity and pore volume calculations. The pore volume can be calculated using the following equation:

$$PV = V - [M / ((1+w) \cdot S \cdot D)]$$

Where PV = pore volume in the column in cubic centimeters
V = the volume of the column packed with waste in cubic centimeters
M = as-packed weight of the waste, including moisture, contained in the column in grams
w = moisture content of the waste contained in the column as a weight ratio from D-2216 (g water/g solids)
S = specific gravity of the waste as determined in D-854 (unitless)
D = density of water in grams per cubic centimeter

The porosity, ϵ , can then be calculated from the following equation:

$$\epsilon = PV/V$$

10.4 Effluent Flow

10.4.1 Once the column is saturated, the testing period should begin. The pressure and/or hydraulic head should be adjusted so that one complete pore volume change is accomplished in 24 hours ± 3 hours. For safety reasons this equipment should not be used at pressures above 50 psig. If the tester has determined that a different pore volume change rate is appropriate for a specific test, a different rate may be used but it must be noted in the report. The effluent flow rate should be determined, recorded, and, if necessary, adjusted at least every third day. All column effluent produced between such determinations should be collected and the quantities reported.

10.4.2 The flow of the water through the column should not be stopped during the entire testing period. If the flow must be stopped for a total of more than one hour in any seven consecutive day testing period, the test must be terminated. The time of occurrence and duration of all flow stoppages must be included in the report.

10.4.3 If the water is found to be channeling through the material or between the column wall and the material, the test should be terminated. Samples obtained prior to the channeling are valid and can be used for testing.

10.4.4 After testing has been initiated, steps should be taken to prevent exposure of the column contents to light except when necessary to check column operation or collect samples. The steps taken shall be included in the report.

10.4.5 Columns are to be run at ambient temperature and at that pressure necessary to maintain flow rates when the column discharge is at or near atmospheric pressure. If, however, the tester



determines that the objectives of the testing are better served by running at a different temperature or pressure, this shall be allowed but the column temperature and pressure must be noted in the report. For safety reasons, this equipment should not be operated above 50 psig.

10.5 Leachate Collection

10.5.1 The column shall be inspected periodically and adjustments made if necessary to maintain the desired operating conditions.

10.5.2 The column shall be operated continuously. A number of pore volumes, sufficient to establish trends and/or steady state conditions in the leachate quality, shall be collected and analyzed. Unless a specific protocol had been previously established, it is recommended that the first, second, fourth, and eighth pore volumes be collected and analyzed. Longer leaching periods can be used if it is necessary to establish trends in the leachate quality over time. Here, it is recommended that the first, second, fourth, eighth, sixteenth, thirty-second, sixty-fourth, one hundred twenty-eighth, etc., pore volumes be analyzed.

10.5.3 Pore volumes are sampled by collecting all column effluent generated over a 24 ± 3 hour or other period corresponding to the pore volume of interest.

10.5.4 Attempts should be made to minimize the column effluent's contact with air. Effluent collection vessels should contain nitrogen-filled head spaces.

10.6 Leachate Sample Preparation

10.6.1 Sample containers will be constructed of materials that do not alter sample quality. Linear polyethylene containers are recommended for samples to be analyzed for index properties or metal ions while glass containers will normally be acceptable for samples to be analyzed for specific organic compounds.

10.6.2 Sample containers will be cleaned according to ASTM Method D-3694, or methods contained in references or as appropriate for the analytes of interest.

10.6.3 Collected pore volumes should be mixed thoroughly before filtration. Contact between the liquid and air should be minimized during this mixing. If there are solids visible in the collected leachate before or after mixing, this shall be noted in the report.

10.6.4 Aliquots of the collected pore volumes will be filtered through a 0.45 micron filter according to ASTM D-1888 within one hour of collection and prior to any analyses except as provided for in 10.7.1. Contact of the sample with air should be minimized before and during filtration.

10.6.5 Samples will be preserved by appropriate methods. Sample preservation techniques are discussed in ASTM D-3694 and references and . Samples to be analyzed for metal ion concentrations can normally be preserved by reducing the sample pH to below 2 using ultrapure nitric acid.

10.6.6 All samples shall be identified as to column source, collection date and time, preservation techniques, and pore volume number.



10.7 Index Properties

10.7.1 A 100 ml aliquot of the unfiltered, unpreserved sample shall be used in measuring pH, conductivity, redox potential, and total dissolved solids according to ASTM methods D-1293, D-1125, D-1498, and D-1888. If any other analyses are performed on this sample, the report must indicate that the sample was unfiltered at the time of analysis.

11. Report

The report shall include the following:

- 11.1 Project identification and description
- 11.2 Description of waste as sampled
- 11.3 Sampling procedures and waste sample handling and storage procedures including the date and time of sampling
- 11.4 All procedures used to prepare the waste for placement in the column including curing procedures and those to alter moisture content or particle size or surface area.
- 11.5 Permeability, particle size and surface area information where available
- 11.6 Temperature used for drying in moisture determination and specific gravity procedures if different than $110 \pm 5^\circ\text{C}$.
- 11.7 Materials used to construct the column apparatus
- 11.8 Column washing procedures
- 11.9 Waste moisture content as sampled and as packed in the column
- 11.10 Characteristics of the waste as placed in the column including specific gravity of the solids, porosity and pore volume.
- 11.11 Weight of the waste placed in the column
- 11.12 Saturation procedures used if different than ASTM D-2434, and date and time that column saturation began and ended
- 11.13 Date and time that leaching begins
- 11.14 Temperature and pressure of column operation at the beginning of the test and at each time samples are collected or flow rates are adjusted
- 11.15 Means used to prevent exposure of column contents to light
- 11.16 Effluent flow rates in pore volumes per day each time measured and the date and time when measured, and all corrections made to flow rates, and quantities of effluent collected between flow rate determinations
- 11.17 The date, time and duration of all flow stoppages
- 11.18 Observations of unusual conditions in the column such as density variations, cracks, gas filled pore spaces, or evidence of fluid channelling along column walls
- 11.19 Date and time that the tester begins and finishes collecting pore volumes, and the number of the pore volume collected.
- 11.20 Type and materials of construction of sampling containers and methods used to clean sample containers
- 11.21 Steps taken to avoid sample contact with air where such steps are called for in the method
- 11.22 Results of measurements of index properties and any other analyses performed on unfiltered samples within one hour of collecting the pore volume from the column. The results of the analyses of that water used to saturate and leach the waste will also be included.



References

- (1) Handbook for Sampling and Sample Preservation of Water and Wastewater, EPA 600/4-82-029, September 1982.



FIGURE 1

SIDE VIEW

TOP VIEW

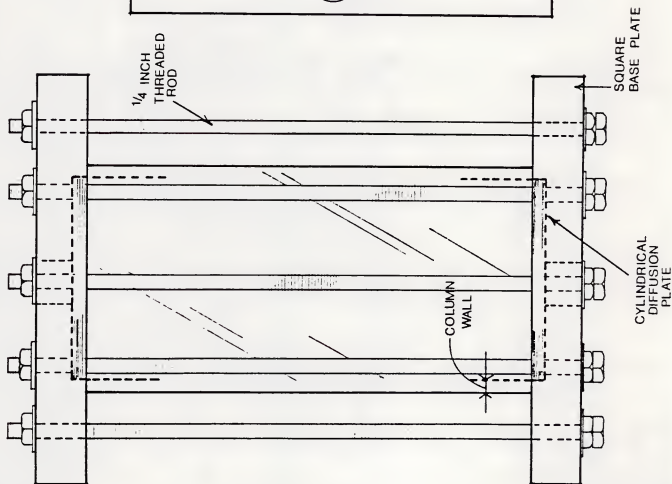
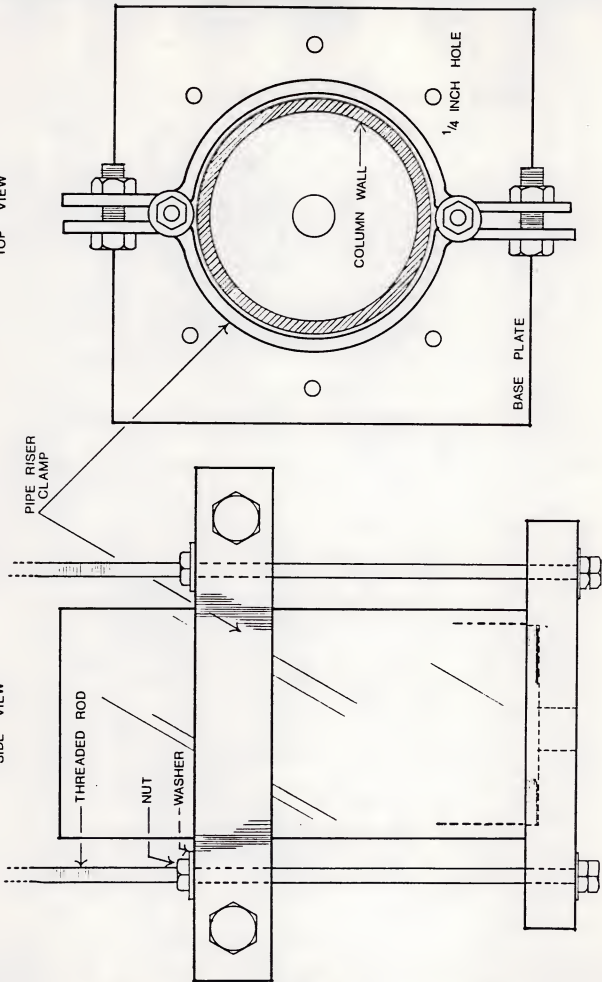




FIGURE 3

SIDE VIEW

TOP VIEW





APPENDIX D

ESTIMATION OF FIELD HYDRAULIC CONDUCTIVITY



ESTIMATION OF FIELD HYDRAULIC CONDUCTIVITY

Two methods were used to estimate soil hydraulic conductivity in the duck pond area. These were:

1. Soil particle analysis
2. Field permeability test

The value chosen for the hydraulic conductivity is important because it impacts calculations of the rate of arsenic mobility.

Soil Particle Analysis

The Fair-Hatch equation (Todd 1959) can be used in conjunction with the grain size analysis to estimate hydraulic conductivity.

$$K = \frac{pg}{u} * \frac{n^3}{(1-n)^2} * \frac{1}{m \left(\frac{\theta}{100} * \frac{p}{d_m} \right)^2} \quad \text{--- (D1)}$$

where: m = A packing factor (found to be 5 experimentally)
 θ = A sand shape factor varying from 6 for spherical grains to 7.7 for angular grains
 p = The percentage of sand held between adjacent sieves
 d_m = The geometric mean of the rated sizes of adjacent sieve
 n = The porosity (20%)
 g = The acceleration due to gravity (980.7 cm/sec²)
 u = The viscosity of the fluid (0.01 g/cm.sec)

Data for the particle size analysis was generated using a wet sieving technique. The distribution is shown in Figure D-1 and calculations required for equation D1 are shown in Table D-1.



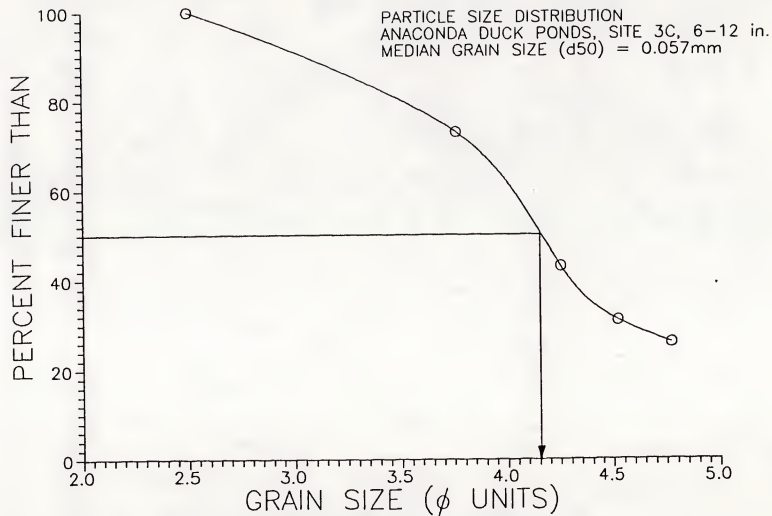


Figure D-1 Particle size distribution of soil from the 6-12 inch layer at site 3C. The median grain size is 0.06 mm.

TABLE D-1

PARTICLE SIZE DISTRIBUTION FOR SOIL 3C FROM THE 6 TO 12-INCH DEPTH

Mesh Size	(mm)	Ø	Soil Weight (g)	P	d _m	P/d _m
80	.177	2.5	5.48	27	0.114	236
200	.074	3.76	5.95	30	0.063	476
270	.053	4.25	2.34	12	0.048	249
325	.044	4.52	0.99	5	0.040	124
400	.037	4.77	0.8			
<400	<.037		4.44			
			Σ = 20	Σ = 1085		

Substituting the appropriate values into equation 1 gives:

$$k = \left(\frac{1.0 * 980.7}{0.01} \right) \left(\frac{0.2^3}{(1-0.2)^2} \right) \left(\frac{1}{5 \left(\frac{6}{100} * 1084.6 \right)^2} \right)$$

$$= 0.06 \text{ cm/sec}$$

This is by necessity an underestimate because the clay fraction (22% of the total soil) is not considered in the denominator P/d_m. Increasing the clay fraction contribution will reduce the hydraulic conductivity.



Field Permeability Test

A percolation test was conducted following protocol established in Cedergren (1967) where:

$$K = \frac{R^2}{2L} * \frac{\ln L}{R} * \frac{\ln h_1/h_2}{\Delta t}$$

where: R = radius of hole (5.1 cm)
L = depth of uncased hole (45.7 cm)
h₁ = depth to water at t₁ (6.25 cm at 2.5 mins.)
h₂ = depth to water at t₂ (10 cm at 7 mins.)

At location 6B a 24-in. deep hole was cased from the top to six inches from the top of the hole to simulate the field hydraulic conductivity once the top six inches had been removed. Figure D-2 shows a plot of head loss with time, between 2.5 to 7 minutes.

$$K = \frac{25.8}{2*45.7} * \frac{\ln 45.7}{5.08} * \frac{\ln 6.25/10}{7-2.5}$$
$$= 0.001 \text{ cm/sec}$$

The permeability (k) is calculated from:

$$k = \frac{Ku}{pg}$$

where: u = the dynamic viscosity (0.01 g/cm₃sec)
p = the density of the fluid (1 g/cm³)
g = the acceleration due to gravity (980.6 cm/sec²)

For this test, $k = 10^{-8} \text{ cm}^2 = 1 \text{ Darcy}$.

This value is consistent with permeabilities measured for sandy soils (Freeze and Cherry 1979, p. 29) and will be the one used to calculate the rate of arsenic migration.



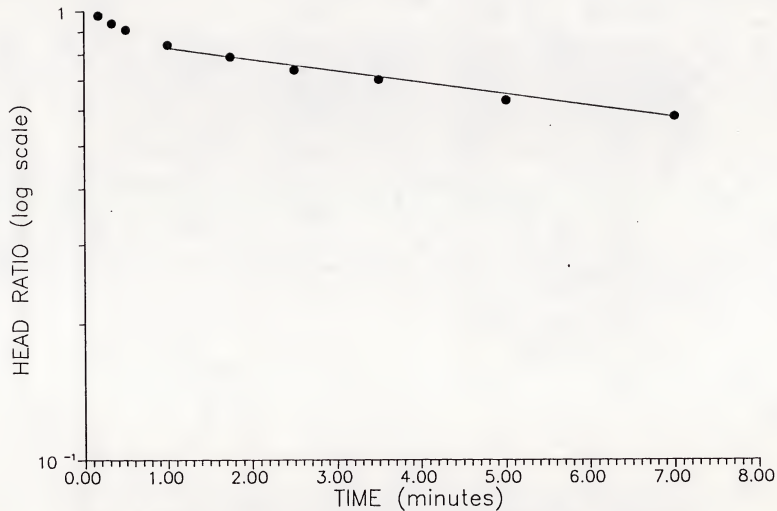


Figure D-2. Results of the field permeability test at location 6B. The hydraulic conductivity between one and seven minutes is 0.001 cm/second.

APPENDIX E

CALCULATION OF COLUMN HYDRAULIC CONDUCTIVITY



ESTIMATION OF COLUMN HYDRAULIC CONDUCTIVITY

Hydraulic conductivity (K) can be calculated from the equation (Freeze and Cherry 1979, p. 335):

$$K = \frac{QL}{AH}$$

where: Q = the steady volumetric discharge through the column
L = the length of the soil sample
A = the cross-sectional area
H = the distance between the fluid surface in the reservoir and the base of the outflow pipe

These quantities are shown schematically in Figure E-1.

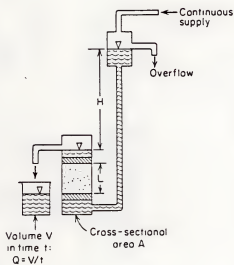


Figure E-1 Schematic of column and supply dimensions (from Freeze and Cherry, 1979)



APPENDIX F

ARSENIC CONCENTRATIONS, pH, SPECIFIC CONDUCTIVITY, AND Eh
AS A FUNCTION OF PORE VOLUMES PASSED IN THE
COLUMN EXPERIMENTS A, D, X, AND Z



COLUMN Z DATA
(3C, 6 to 12-Inch Horizon)

Pore Volume	As (ug/L)	pH (s.u.)	Sp. Cond. (umhos/cm)	Eh (millivolts)
1	380	7.8	2560	+330
3	550	7.7	2480	+330
5.7	900	7.8	1367	+320
8.3	3200	8.2	730	+335
10.2	3000	8.1	738	+370
11.7	2720	8.1	746	+355
14	1700	7.8	780	+310
17.6	840	7.8	782	---
20	560	8.1	707	+340

--- not recorded



COLUMN X DATA
(3C, 12 to 36-Inch Horizon)

Pore Volume	As (ug/L)	pH (s.u.)	Sp. Cond. (umhos/cm)	Eh (millivolts)
1	11	8.1	6410	+320
4.5	6.5	7.8	1986	+355
17	2.6	8.1	958	+310
28	3.2	8.2	628	+400
35	8.2	8.3	619	+375
44	22	8.1	658	+370
51.2	19	8.1	654	+295
61	26	--	--	--
68	23	8.0	601	+400
80	21	--	--	--
88	20	8.1	600	+395
95	25	--	--	--
109	23	7.8	595	+400

--- not recorded



COLUMN A DATA

Pore Volume	As (ug/L)	pH (s.u.)	Sp. Cond. (umhos/cm)	Eh (millivolts)
0.1	16.0	7.3	14750	+225
1.0	9.7	6.9	6730	+115
2.6	17	7.5	2560	+145
7	100	7.7	1045	+150
11	440	7.9	1043	+225
14.6	490	7.4	887	+90
17.9	240	7.7	920	+365
20.7	220	7.7	916	+365
23.2	160	7.9	959	+315
25.4	160	7.9	894	+370
26.7	180	7.8	1000	+370
29.3	190	7.7	1028	+370
33.5	180	--	--	--
36.4	190	--	--	--
38.5	120	7.8	991	+230



COLUMN D DATA
(3C, 12 to 18-Inch Horizon)

Pore Volume	As (ug/L)	pH (s.u.)	Sp. Cond. (umhos/cm)	Eh (millivolts)
0.8	20	7.7	4570	+355
1.1	10	8.1	3820	+330
2.2	16	7.7	3230	+370
5	42	8.0	2580	+350
6.2	62	8.2	2290	+390
6.8	71	8.0	2410	+360
8.2	93	--	--	--
9.7	66	7.9	1780	--
13	59	7.9	1380	--
15.7	49	7.9	766	+400
18.8	35	--	--	--
23.9	94 ^a	7.9	642	+400
26.4	95 ^a	7.9	685	+340

^a Hydraulic conductivity decreased due to clogging of cores. The residence time of fluid in the cores tripled resulting in higher arsenic concentrations.

-- not recorded



APPENDIX G

ARSENIC CONCENTRATIONS IN THE SUPERNATANT GENERATED
DURING THE SORPTION TEST



SORPTION TEST DATA

(12.5g/250 mL)

Soil	As conc. Spike (ug/L)	As conc.	
		24 hours	48 hours
3C 12-18 inches (8 ug/g)	0	13	9
	16	17	11
	31	26	18
	58	35	29
50 mL removed after 24 hours from initial 25 mL			
	Blank (0)		310
3C 6-12 inches (30 ug/g)	100		360
	250		440
	500		560
250 mL of fluid used.			



APPENDIX H

MEASURED DEPTHS OF PRE-DRILLED BORES



MEASURED DEPTHS OF PRE-DRILLED BORES

	<u>Total Depth</u>	<u>Average</u>
<u>SITE 4D</u>		
6 - 12 inches	12, 12, 12, 12.75, 12.5	12.25
12 - 18 inches	17, 18, 18, 18.5	17.9
<u>SITE 5C</u>		
6 - 12 inches	12, 12, 11.5, 12, 12.25	11.95
12 - 18 inches	18, 18.25, 18.25, 18.5, 18	18.2
<u>SITE 1F</u>		
12 - 18 inches	18, 18, 18.5, 19	18.4



APPENDIX I-1

SPECIATION OF INPUT MIX WATER



ANACONDA DUCK PONDS ANALYSIS.
SPECIATION AND SI RUN. 11/10/86. AD.

20.00 MG/L .00
0 1 0 2 0 0 0 0
0 .00 .00 .00
330 .000E+00 -6.90
61 5.000E-03 -13.00
150 1.120E+02 -2.00
281 1.500E-01 -14.00
500 1.300E+01 -3.00
140 1.220E+02 -6.00
732 1.170E+02 -2.00
460 2.050E+01 -3.00
H2O HAS BEEN INSERTED AS A COMPONENT
3 1
330 6.900E+00 .00

CHARGE BALANCE: UNSPECIATED

SUM OF CATIONS = 7.852E-03 SUM OF ANIONS = 6.504E-03
PERCENT DIFFERENCE = 9.384832 (CATIONS-ANIONS)/(CATIONS+ANIONS)

ITERATIONS DURING SOLVE

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY
1	MG	8.435E-04	1.899E-03	-3.00000
2	MG	8.435E-04	3.181E-04	-3.14496
3	MG	8.435E-04	3.451E-04	-3.16173
4	MG	8.435E-04	6.481E-06	-3.27524
5	MG	8.435E-04	-5.786E-06	-3.27541

OUTPUT DATA: ITERATIONS = 5

ID	NAME	ANAL MOL	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA
460	MG	8.435E-04	7.764E-04	5.339E-04	-3.27257	.688
61	H3ASO4	3.524E-08	2.351E-13	2.356E-13	-12.62776	1.002
150	CA	2.795E-03	2.555E-03	1.747E-03	-2.75775	.684
281	FE+3	2.687E-06	3.680E-14	1.654E-14	-13.78136	.450
500	NA	5.657E-04	5.636E-04	5.100E-04	-3.29241	.905
140	CO3	2.034E-03	7.015E-07	4.748E-07	-6.32349	.677
732	SO4	1.218E-03	9.451E-04	6.292E-04	-3.20122	.666
2	H2O	.000E+00	-5.685E-06	9.999E-01	-.00006	1.000
330	H	.000E+00	-2.455E-03	1.259E-07	-6.90000	.915

SPECIES: TYPE I - COMPONENTS

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
460	MG	7.764E-04	5.339E-04	-3.27257	.688	.163
61	H3ASO4	2.351E-13	2.356E-13	-12.62776	1.002	-.001
150	CA	2.555E-03	1.747E-03	-2.75775	.684	.165
281	FE+3	3.680E-14	1.654E-14	-13.78136	.450	.347
500	NA	5.636E-04	5.100E-04	-3.29241	.905	.043
140	CO3	7.015E-07	4.748E-07	-6.32349	.677	.170
732	SO4	9.451E-04	6.292E-04	-3.20122	.666	.177



SPECIES:		TYPE II - COMPLEXES					
ID	NAME	CALC MOL	ACTIVITY	LOG ACTVITY	GAMMA	NEW LOGK	
3301401	KH2CO3 AQ	4.288E-04	4.298E-04	-3.36674	1.002	16.756	
3307320	KHSO4 -	7.404E-09	6.699E-09	-8.17399	.905	1.971	
3300020	K OH-	6.023E-08	5.434E-08	-7.26489	.902	-14.120	
4603300	KMGOH +	4.919E-09	4.475E-09	-8.34925	.910	-11.935	
4601400	KMGC03 AQ	2.235E-07	2.240E-07	-6.64968	1.002	2.945	
4601401	KMGHCO3 +	9.496E-06	8.580E-06	-5.06653	.903	11.474	
4607320	KMGSO4 AQ	5.725E-05	5.737E-05	-4.24128	1.002	2.232	
1503300	KCAOH +	2.536E-09	2.304E-09	-8.63751	.908	-12.738	
1501400	KCAHCO3 +	2.433E-05	2.210E-05	-4.65557	.908	11.367	
1501401	KCAC03 AQ	1.059E-06	1.061E-06	-5.97415	1.002	3.106	
1507320	KCAS04 AQ	2.141E-04	2.146E-04	-3.66835	1.002	2.290	
5001400	KNAC03 -	3.829E-09	3.473E-09	-8.45930	.907	1.199	
5001401	KNAHCO3 AQ	3.657E-07	3.665E-07	-6.43590	1.002	10.079	
5007320	KNAS04 -	1.717E-06	1.557E-06	-5.80764	.907	.728	
2813300	KFEOH +2	9.332E-10	6.289E-10	-9.20142	.674	-2.149	
2817320	KFES04 +	8.539E-14	7.736E-14	-13.11146	.906	3.914	
2813301	KFEOH2 +	2.460E-06	2.231E-06	-5.65147	.907	-5.628	
2813302	KFEOH3 AQ	2.077E-07	2.082E-07	-6.68152	1.002	-13.601	
2813303	KFEOH4 -	1.823E-08	1.654E-08	-7.78158	.907	-21.558	
2817321	KFE(SO4)2 -	1.669E-15	1.509E-15	-14.82131	.904	5.406	
2813304	KFE2(OH)2+4	6.604E-17	1.313E-17	-16.88160	.199	-2.417	
2813305	KFE3(OH)4+5	7.462E-20	5.983E-21	-20.22307	.080	-5.383	
3300611	KH2ASO4 -	1.242E-08	1.123E-08	-7.94963	.904	-2.178	
3300612	KHASO4 -2	2.281E-08	1.523E-08	-7.81726	.668	-8.814	
3300613	KASO4 -3	6.713E-13	2.706E-13	-12.56764	.403	-20.245	
3301400	KHCO3 -	1.569E-03	1.423E-03	-2.84685	.907	10.419	

SPECIES:		TYPE III - FIXED SOLIDS					
ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH		
2	H2O	-5.685E-06	-5.245	.000	.000		
330	H	-2.455E-03	-2.610	6.900	.000		

SPECIES:		TYPE VI - SPECIES NOT CONSIDERED					
ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH		
3301403	CO2(GAS)	1.105E-02	-1.957	18.167	-.530		



PERCENTAGE DISTRIBUTION OF COMPONENTS

3	92.1	PERCENT BOUND IN SPECIES #	460	MG
	1.1	PERCENT BOUND IN SPECIES #	4601401	KMGHCO3 +
	6.8	PERCENT BOUND IN SPECIES #	4607320	KMGSO4 AQ
H3ASO4	35.3	PERCENT BOUND IN SPECIES #	3300611	KH2ASO4 -
	64.7	PERCENT BOUND IN SPECIES #	3300612	KHASO4 -2
CA	91.4	PERCENT BOUND IN SPECIES #	150	CA
	7.7	PERCENT BOUND IN SPECIES #	1507320	KCASO4 AQ
FE+3	91.6	PERCENT BOUND IN SPECIES #	2813301	KFEOH2 +
	7.7	PERCENT BOUND IN SPECIES #	2813302	KFEOH3 AQ
NA	99.6	PERCENT BOUND IN SPECIES #	500	NA
CO3	21.1	PERCENT BOUND IN SPECIES #	3301401	KH2CO3 AQ
	1.2	PERCENT BOUND IN SPECIES #	1501400	KCAHCO3 +
	77.1	PERCENT BOUND IN SPECIES #	3301400	KHCO3 -
SO4	77.6	PERCENT BOUND IN SPECIES #	732	SO4
	4.7	PERCENT BOUND IN SPECIES #	4607320	KMGSO4 AQ
	17.6	PERCENT BOUND IN SPECIES #	1507320	KCASO4 AQ
H2O	1.1	PERCENT BOUND IN SPECIES #	3300020	K OH-
	86.5	PERCENT BOUND IN SPECIES #	2813301	KFEOH2 +
	11.0	PERCENT BOUND IN SPECIES #	2813302	KFEOH3 AQ
	1.3	PERCENT BOUND IN SPECIES #	2813303	KFEOH4 -
H	34.9	PERCENT BOUND IN SPECIES #	3301401	KH2CO3 AQ
	63.9	PERCENT BOUND IN SPECIES #	3301400	KHCO3 -

IDX	NAME	AQUEOUS MASS	SORBED MASS
460	MG	8.433E-04	.000E+00
61	H3ASO4	3.523E-08	.000E+00
150	CA	2.795E-03	.000E+00
281	FE+3	2.687E-06	.000E+00
500	NA	5.656E-04	.000E+00
140	CO3	2.034E-03	.000E+00
732	SO4	1.218E-03	.000E+00
2	H2O	5.685E-06	.000E+00
330	H	2.455E-03	.000E+00



CHARGE BALANCE: SPECIATED

SUM OF CATIONS = 7.263E-03 SUM OF ANIONS 3.462E-03

PERCENT DIFFERENCE = 35.441850 (CATIONS-ANIONS)/(CATIONS+ANIONS)

NONCARBONATE ALKALINITY = .000E+00

IONIC STRENGTH = .009642

SATURATION INDICES FOR ALL MINERALS AND SOLIDS

ID	NAME	LOG SI	LOG K	MIN LOGK	MAX LOGK	LOG IAP
6015000	ANHYDRITE	-1.369	4.590	-.047	-.047	-5.959
5015000	ARAGONITE	-.790	8.292	-.033	-.033	-9.081
5046000	ARTINITE	-9.028	-9.959	-.359	-.359	.931
2046000	BRUCITE	-6.588	-17.115	-.323	-.323	10.527
5015001	CALCITE	-.635	8.446	8.528	-.032	-9.081
5015002	DOLOMITE	-1.781	16.896	-.104	-.104	-18.677
6046000	EPSOMITE	-4.299	2.175	.035	.035	-6.474
2028119	FE(OH)3 NBS	3.488	-3.430	.000	.000	6.918
2028100	FERRIHYDRITE	2.027	-4.891	-1.557	-4.996	6.918
6028100	FE2(SO4)3	-41.485	-4.319	-.089	-.739	-37.166
2028102	GOETHITE	6.238	-.681	-.181	-.181	6.919
6015001	GYP SUM	-1.108	4.851	.003	.003	-5.959
2028105	HEMATITE	17.460	3.622	-.386	-.386	13.837
5015003	HUNTITE	-8.223	29.646	-.322	-.322	-37.869
5046001	HYDRMAGNESIT	-19.744	8.113	-.653	-.653	-27.857
6050000	JAROSITE NA	1.108	10.748	-.452	-.452	-9.639
6028101	JAROSITE H	-1.836	11.411	-.689	-.689	-13.247
2028104	MAGHEMITE	7.451	-6.386	.000	.000	13.837
5046002	MAGNESITE	-1.644	7.952	8.202	7.702	-9.596
6050001	MIRABILITE	-8.435	1.351	.237	.237	-9.787
3050000	NATRON	-11.401	1.508	.197	.197	-12.909
5046003	NESQUEHONITE	-4.048	5.549	5.061	4.474	-9.596
6050002	THENARDITE	-9.614	.172	-.007	-.007	-9.786
5050001	THERMONATR	-13.068	-.160	-.035	-.035	-12.908
3006100	AS2O5	-32.022	-6.767	-.068	-9.546	-25.255
7215000	CA3(ASO4)26W	-14.429	-22.300	.000	.000	7.871
7228100	FEASO4.2W	-6.109	-.400	.000	.000	-5.709
2015000	LIME	-22.333	-33.375	-.578	-.578	11.042
2015001	PORTLANDITE	-12.017	-23.059	-.384	-.384	11.042
2046001	PERICLASE	-11.434	-21.962	-.452	-.452	10.527
3046001	MAG-FERRITE	6.766	-17.598	-.833	-.833	24.364
2028103	LEPIDOCROCIT	5.548	-1.371	.000	.000	6.919
5015007	MG-CALCITE	-1.133	8.000	.000	.000	-9.133



APPENDIX I-2

EQUILIBRIATION RUN BETWEEN A MINERAL SUITE
AND INPUT MIX WATER



T = 20.00 MG/L .00
 0 0 1 0 2 0 0 0 0
 0 .00 .00 .00 .00

330 .000E+00 -6.90
 61 5.000E-03 -13.00
 150 1.120E+02 -2.00
 281 1.500E-01 -14.00
 500 1.300E+01 -3.00
 140 1.220E+02 -6.00
 732 1.170E+02 -2.00
 460 2.050E+01 -3.00

H2O HAS BEEN INSERTED AS A COMPONENT

3 4
 330 6.900E+00 .00
 6015001 .000E+00 .00
 5015002 .000E+00 .00
 5015001 .000E+00 .00

CHARGE BALANCE: UNSPECIATED

SUM OF CATIONS= 7.852E-03

SUM OF ANIONS = 6.504E-03

PERCENT DIFFERENCE = 9.384832 (CATIONS-ANIONS)/(CATIONS+ANIONS)

ITERATIONS DURING SOLVE

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVITY
1	SO4	-3.868E-04	1.756E-02	-2.00000
2	SO4	-3.868E-04	-7.201E-03	-2.63790
3	SO4	-3.868E-04	-4.614E-03	-2.48277
4	SO4	-3.868E-04	-6.344E-04	-2.40784
5	SO4	-3.868E-04	-2.349E-05	-2.39757
6	H3ASO4	3.524E-08	1.984E-10	-12.74513
7	H3ASO4	3.524E-08	4.910E-11	-12.74757

OUTPUT DATA: ITERATIONS = 7

ID	NAME	ANAL MOL	CALC MOL	ACTIVITY	LOG ACTVITY	GAMM
732	SO4	1.218E-03	8.892E-03	4.007E-03	-2.39714	.451
61	H3ASO4	3.524E-08	1.766E-13	1.786E-13	-12.74817	1.011
500	NA	5.657E-04	5.543E-04	4.584E-04	-3.33871	.827
281	FE+3	2.687E-06	6.167E-14	1.528E-14	-13.81574	.248
150	CA	2.795E-03	7.045E-03	3.516E-03	-2.45401	.499
330	H	.000E+00	-5.747E-03	1.259E-07	-6.90000	.856
140	CO3	2.034E-03	2.125E-06	1.019E-06	-5.99202	.479
460	MG	8.435E-04	6.828E-03	3.481E-03	-2.45830	.510
2	H2O	.000E+00	2.552E-02	9.999E-01	-.00006	1.000

SPECIES: TYPE I - COMPONENTS

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVITY	GAMMA	NEW I
460	MG	6.828E-03	3.481E-03	-2.45830	.510	.29
61	H3ASO4	1.766E-13	1.786E-13	-12.74817	1.011	-.00
150	CA	7.045E-03	3.516E-03	-2.45401	.499	.30
281	FE+3	6.167E-14	1.528E-14	-13.81574	.248	.60
500	NA	5.543E-04	4.584E-04	-3.33871	.827	.08
140	CO3	2.125E-06	1.019E-06	-5.99202	.479	.31
732	SO4	8.892E-03	4.007E-03	-2.39714	.451	.34



SPECIES:	TYPE II - COMPLEXES				
ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA
3301401	KH2CO3 AQ	9.119E-04	9.220E-04	-3.03527	1.011
3307320	KHSO4 -	5.174E-08	4.267E-08	-7.36991	.825
3300020	K OH-	6.663E-08	5.434E-08	-7.26489	.816
4603300	KMGOH +	3.472E-08	2.918E-08	-7.53499	.840
4601400	KMGCO3 AQ	3.099E-06	3.134E-06	-5.50395	1.011
4601401	KMGHCO3 +	1.463E-04	1.200E-04	-3.92080	.820
4607320	KMGSO4 AQ	2.357E-03	2.383E-03	-2.62293	1.011
1503300	KCAOH +	5.542E-09	4.637E-09	-8.33378	.837
1501400	KCAHCO3 +	1.140E-04	9.542E-05	-4.02037	.837
1501401	KCACO3 AQ	4.532E-06	4.582E-06	-5.33894	1.011
1507320	KCASO4 AQ	2.721E-03	2.751E-03	-2.56053	1.011
5001400	KNACO3 -	8.048E-09	6.697E-09	-8.17414	.832
5001401	KNAHCO3 AQ	6.990E-07	7.067E-07	-6.15074	1.011
5007320	KNASO4 -	1.071E-05	8.915E-06	-5.04986	.832
2813300	KFEOH +2	1.231E-09	5.810E-10	-9.23579	.472
2817320	KFES04 +	5.492E-13	4.552E-13	-12.34176	.829
2813301	KFEOH2 +	2.477E-06	2.061E-06	-5.68585	.832
2813302	KFEOH3 AQ	1.902E-07	1.924E-07	-6.71590	1.011
2813303	KFEOH4 -	1.836E-08	1.528E-08	-7.81596	.832
2817321	KFE(SO4)2 -	6.856E-14	5.656E-14	-13.24752	.825
2813304	KFE2(OH)2+4	2.440E-16	1.121E-17	-16.95035	.046
2813305	KFE3(OH)4+5	5.808E-19	4.718E-21	-20.32620	.008
3300611	KH2ASO4 -	1.032E-08	8.511E-09	-8.07004	.825
3300612	KHASO4 -2	2.493E-08	1.154E-08	-7.93767	.463
3300613	KASO4 -3	1.160E-12	2.051E-13	-12.68805	.177
3301400	KHCO3 -	3.65E-05	2.180E-05	-4.66148	.837
3301401	KH2CO3 AQ	3.788E-08	3.826E-08	-7.41724	1.010

SPECIES:	TYPE III - FIXED SOLIDS				
ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2	H2O	2.900E-02	-1.538	.000	.000
5015001	CALCITE	1.594E-02	-1.797	8.446	2.585
5015002	DOLOMITE	-6.973E-03	-2.157	16.896	8.290
6015001	GYPSUM	-1.452E-02	-1.838	4.851	-2.261

SPECIES:	TYPE VI - SPECIES NOT CONSIDERED				
ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
3301403	CO2(GAS)	9.833E-07	-6.007	18.167	-.530

PERCENTAGE DISTRIBUTION OF COMPONENTS

H

>1000.	PERCENT BOUND IN SPECIES #3300020	K OH-
>1000.	PERCENT BOUND IN SPECIES #4603300	KMGOH +
>1000.	PERCENT BOUND IN SPECIES #1503300	KCAOH +
>1000.	PERCENT BOUND IN SPECIES #2813301	KFEOH2 +
>1000.	PERCENT BOUND IN SPECIES #2813302	KFEOH3 AQ
>1000.	PERCENT BOUND IN SPECIES #2813303	KFEOH4 -
29.7	PERCENT BOUND IN SPECIES #3300611	KH2ASO4 -
>1000.	PERCENT BOUND IN SPECIES #3300612	KHASO4 -2
282.8	PERCENT BOUND IN SPECIES #3300613	KASO4 -3



H3ASO4 99.0 PERCENT BOUND IN SPECIES #3300612 KHASO4 -2

CA 67.3 PERCENT BOUND IN SPECIES # 150 CA
32.6 PERCENT BOUND IN SPECIES #1507320 KCASO4 AQ

FE+3 5.7 PERCENT BOUND IN SPECIES #2813302 KFEOH3 AQ
93.9 PERCENT BOUND IN SPECIES #2813303 KFEOH4 -

NA 97.7 PERCENT BOUND IN SPECIES # 500 NA
2.3 PERCENT BOUND IN SPECIES #5007320 KNASO4 -

SO4 67.6 PERCENT BOUND IN SPECIES # 732 SO4
15.0 PERCENT BOUND IN SPECIES #4607320 KMGSO4 AQ
17.3 PERCENT BOUND IN SPECIES #1507320 KCASO4 AQ

CO3 6.8 PERCENT BOUND IN SPECIES # 140 CO3
8.2 PERCENT BOUND IN SPECIES #4601400 KMGC03 AQ
2.2 PERCENT BOUND IN SPECIES #4601401 KMGHC03 +
1.7 PERCENT BOUND IN SPECIES #1501400 KCAHCO3 +
12.0 PERCENT BOUND IN SPECIES #1501401 KCACO3 AQ
68.9 PERCENT BOUND IN SPECIES #3301400 KHC03 -

MG 69.7 PERCENT BOUND IN SPECIES # 460 MG
30.2 PERCENT BOUND IN SPECIES #4607320 KMGSO4 AQ

H2O 41.3 PERCENT BOUND IN SPECIES #3300020 K OH-
17.5 PERCENT BOUND IN SPECIES #4603300 KMGOH +
2.8 PERCENT BOUND IN SPECIES #1503300 KCAOH +
1.7 PERCENT BOUND IN SPECIES #2813302 KFEOH3 AQ
36.6 PERCENT BOUND IN SPECIES #2813303 KFEOH4 -

IDX	NAME	AQUEOUS MASS	SORBED MASS
330	H	-2.874E-10	.000E+00
61	H3ASO4	3.524E-08	.000E+00
150	CA	8.343E-03	.000E+00
281	FE+3	2.687E-06	.000E+00
500	NA	5.657E-04	.000E+00
732	SO4	1.573E-02	.000E+00
140	CO3	3.780E-05	.000E+00
460	MG	7.816E-03	.000E+00
2	H2O	2.757E-05	.000E+00

CHARGE BALANCE: SPECIATED

SUM OF CATIONS = 2.268E-02 SUM OF ANIONS 2.134E-02

PERCENT DIFFERENCE = 3.059093 (CATIONS-ANIONS)/(CATIONS+ANION)



NONCARBONATE ALKALINITY = .000E+00
 IONIC STRENGTH = .043708

SATURATION INDICES FOR ALL MINERALS AND SOLIDS

ID	NAME	LOG SI	LOG K
6015000	ANHYDRITE	-.261	4.590
5015000	ARAGONITE	-.154	8.292
5046000	ARTINITE	-2.686	-9.959
2046000	BRUCITE	-1.391	-17.115
5015001	CALCITE	.000	8.446
5015002	DOLOMITE	.000	16.896
6046000	EPSOMITE	-2.681	2.175
2028119	FE(OH)3 NBS	3.359	-3.430
2028100	FERRIHYDRITE	1.898	-4.891
6028100	FE2(SO4)3	-52.479	-4.319
2028102	GOETHITE	6.108	-.681
6015001	GYPSUM	.000	4.851
2028105	HEMATITE	17.200	3.622
5015003	HUNTITE	-4.151	29.646
5046001	HYDRMAGNESIT	-9.965	8.113
6050000	JAROSITE NA	-4.246	10.748
6028101	JAROSITE H	-9.381	11.411
2028104	MAGHEMITE	7.192	-6.386
5046002	MAGNESITE	-.498	7.952
6050001	MIRABILITE	-7.632	1.351
3050000	NATRON	-11.070	1.508
5046003	NESQUEHONITE	-2.902	5.549
6050002	THENARDITE	-8.810	.172
5050001	THERMONATR	-12.737	-.160
3006100	AS2O5	-40.893	-6.767
7215000	CA3(ASO4)26W	-9.243	-22.300
7228100	FEASO4.2W	-10.675	-.400
2015000	LIME	-17.647	-33.375
2015001	PORTLANDITE	-7.331	-23.059
2046001	PERICLASE	-6.238	-21.962
3046001	MAG-FERRITE	11.703	-17.59

